PEROXIDE CURABLE BUTYL RUBBER DERIVATIVES

By

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ABSTRACT:

Solid-state rheometry and model compound reactions are used to investigate free radical reactions of *N*-arylmaleimide coagents with saturated and unsaturated polymers. N,N′-*m*-phenylene dimaleimide (BMI) is shown to provide superior cross-link densities over diacrylate and diallyl coagents for all of the polymers studied, including linear low density polyethylene (LLDPE), poly(ethylene oxide) (PEO), cis-poly(butadiene) (PBD) and cis-poly(isoprene) (PIP). Studies of the *N*-phenylmaleimide (NPM) + cis-cyclooctane system show that C–H bond addition to yield *N*-aryl-2-alkylsuccinimide grafts is the predominant reaction pathway, as opposed to maleimide homopolymerization. In contrast, peroxide-initiated reactions of cis-cyclooctene with small NPM concentrations generate highly alternating poly(cyclooctene-alt-*N*-phenylmaleimide) in high yield, indicating that unsaturated mers in materials such as PBD engage maleimides in an efficient alternating copolymerization between electron-rich and electron-deficient monomer pairs. Factors that affect the reactivity of different polymers in these C–H bond additions and alternating copolymerizations are discussed.

Isobutylene-rich elastomers bearing functional groups that engage N-arylmaleimides in C-H bond addition and/or alternating copolymerization are described. While inactive to cross-linking when treated at high temperature with peroxide alone, these co-curing elastomers can be cross-linked substantially when combined with bis-maleimide coagents such as N,N′-*m*-phenylene dimaleimide (BMI). Poly(isobutylene-co-isoprene) (IIR) samples containing relatively high amounts of residual isoprene unsaturation are shown to provide relatively low coagent cure reactivity, whereas IIR derivatives bearing pendant polyether or vinyl ether functionality are shown to provide exceptional cross-linking rates and extents when treated with identical BMI formulations. The design of such co-curing elastomers is discussed, along with the physical properties of the resulting vulcanizates.

Isobutylene rich elastomers bearing oligomerizable (C=C) functional groups, macromonomers, that are activated in the presence of free-radical initiators are described. The criteria for determining the macromonomers that are best suited for preparing thermosets of IIR is discussed. While IIR derivatives bearing pendant acrylic, styrenic and maleimide functionality are shown to provide exceptional cross-linking rates and extents, they are also shown to suffer from instability in the absence of peroxide. IIR carrying pendant methacrylic and itaconate functionality are shown to provide a good balance of cure rates and stability. Nitroxyl based radical trap that provides scorch protection to the macromonomers while regenerating the cure extent is discussed.

Functional macromonomer derivatives of IIR bearing containing multi-functional pendant groups are discussed. IIR derivatives with itaconate and low amounts of BHT pendant groups is shown to act as bound anti-oxidant while IIR containing pendant fluoro groups are shown to have reduced surface energy. Ionic coagents are used to cross-link IIR containing itaconate pendant groups and their physical properties are discussed.

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AA - Acrylate

AO - Anti-oxidant

AOTEMPO - 4-Acryloyl- (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl

BDE - Bond dissociation energy

BHT - 2,6-di-*tert*-butyl-4-methylphenol

BIIR - Brominated poly(isobutylene-*co*-isoprene)

BMI - N,N'-*m*-Phenylene dimaleimide

Bu_4NBr - Tetrabutylammonium bromide

Bu_4NOAc - Tetrabutylammonium acetate

Bu_4NOH - Tetrabutylammonium hydroxide

CIIR - Chlorinated poly(isobutylene-*co*-isoprene)

CyOc - Cyclooctane

DAIP - Diallyl isophthalate

DCP - Dicumyl peroxide

DDI - Dodecyl itaconate

DDMA - Dodecyl maleate

DSC - Differential scanning calorimetry

EPDM - Ethylene propylene diene monomer rubber

EPR - Ethylene propylene rubber

GC - Gas chromatography

HNBR - Hydrogenated nitrilebutadiene rubber

HPLC - High performance liquid chromatography

IIR - Poly(isobutylene-*co*-isoprene)

IP - Isoprene

ITA - Itaconate

LLDPE - Linear low density polyethylene

NDA - Neopentylglycol diacrylate

NMR - Nuclear magnetic resonance

NPM - N-Phenyl maleimide

MAA - Methacrylate

MBA - Maleimidobenzoate

MS - Mass spectrometry

PTC - Phase transfer catalysis

PBD - *Cis*-polybutadiene

PE - Polyethylene

PEG - Polyethylene glycol

PEO - Polyethylene oxide

PIB - Polyisobutylene

PIP - *Cis*-Polyisoprene

PVC - Polyvinyl chloride

SUC - Succinate

TBAB - Tetrabutylammonium bromide

TEMPO - (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl

UA - Undecenoate

VBA - Vinylbenzoate

Chapter 1 : Introduction

1.1 Cross-linking of Polymers

Linear and branched elastomers exhibit viscoelastic behavior, such that the application of a stress results in polymer chain relaxation. In other words, imposing mechanical stress on an elastomer will result in relaxation, due to the large-scale mobility of polymer chains. In an amorphous, uncross-linked polymer that is above its glass transition temperature, the ability to resist deformation is directly proportional to the entanglements of the constituting polymeric chains.[1] But these entanglements or junctures are not permanent, and the polymer cannot sustain its resistance to deformation. This behaviour makes the polymers unsuitable for applications requiring dimensional stability under prolonged periods of stress. Such dimensional stability can be achieved by creating thermosets of polymers through cross-linking processes, which generate three dimensional networks within the polymer matrix that are permanent. These three dimensional networks then hold the chains in place when subjected to prolonged stresses, thereby imparting the required stability.

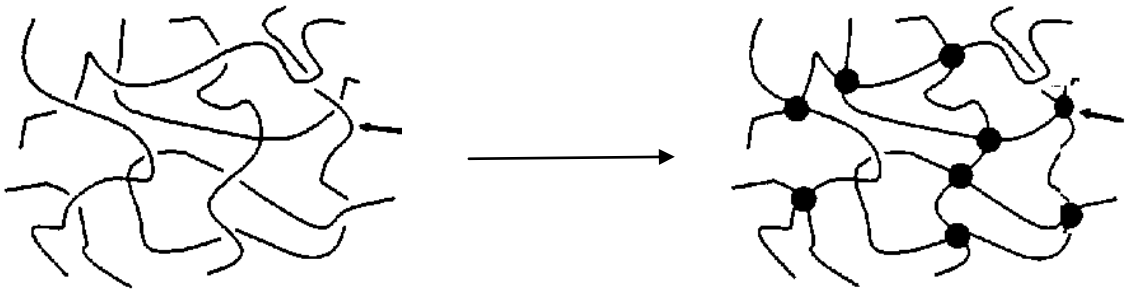


Figure 1.1: Crosslinking of polymer chains

For example, low density polyethylene (LDPE), when converted to a cross-linked thermoset, exhibits an increase in the stress crack resistance.[2] Polyvinyl chloride (PVC) samples containing alkoxysilane grafts have been cross-linked through moisture-curing chemistry to improve the Young's modulus and

elongation at break of the material.[3] Natural rubber formulations containing sulphur curatives provide superior modulus (300%) and flex fatigue values when compared to their uncured parent materials.[4]

1.2 Cross-linking Technology

The formation of three dimensional network structures within a polymer is achieved through reactions that introduce covalent bonds between polymer chains. Such chemical reactions can be brought about by several techniques. Two of the dominant methods of cross-linking polymers are sulphur vulcanization and peroxide curing.

Sulphur vulcanization was first introduced by Charles Goodyear in 1841 and Thomas Hancock in 1842,[4] while peroxide cross-linking was not known until Ostromislensky introduced the technology in 1915.[5] Despite the fact that sulphur vulcanization has been around for more than 150 years, the mechanism behind the vulcanization reaction is not well understood as both free-radical[6] and ionic mechanisms[7] have been suggested. Regardless of the underlying mechanism(s), sulphur vulcanization invariably creates C-S bonds whose bond strength is reported to be 285 kJ/mol, as well as polysulphide bonds with strengths on the order of just 267 kJ/mol.[10] These vulcanizates provide good mechanical properties, particularly when subjected to dynamic loads, and are valued in applications where flex fatigue or heat buildup are key design variables. However, the relative weakness of polysulfidic cross-links tends to result in poor long term aging and stress relaxation performance.

In the early years of sulphur cure technology, formulations had high sulphur concentrations and required relatively high temperatures. To accelerate the curing process and support milder reaction conditions, organic accelerators like guanidines, dithiocarbamic acid and mercaptobenzothiazole were introduced.[8,9] This was followed by formulations that included zinc oxide and stearic acid as sulphur-cure formulation activators.[4] Unfortunately, sulphur-cured thermosets are malodourous due to sulphur-based reaction by-products, and they can contain leachable and extractable compounds that present a

hazard to human health. As such, sulphur-cured products are unsuitable for medical and food grade applications.

Peroxide cures, on the other hand, generate C-C cross-links with bond strength of approximately 351kJ/mol. As a result, polymers cross-linked by peroxides tend to provide superior heat aging and compression set resistance.[10] The amount and toxicity of peroxide cure by-products are also considerably less than sulfur-cure formulations, thereby facilitating their use in applications where extractables and leachables are of particular concern.

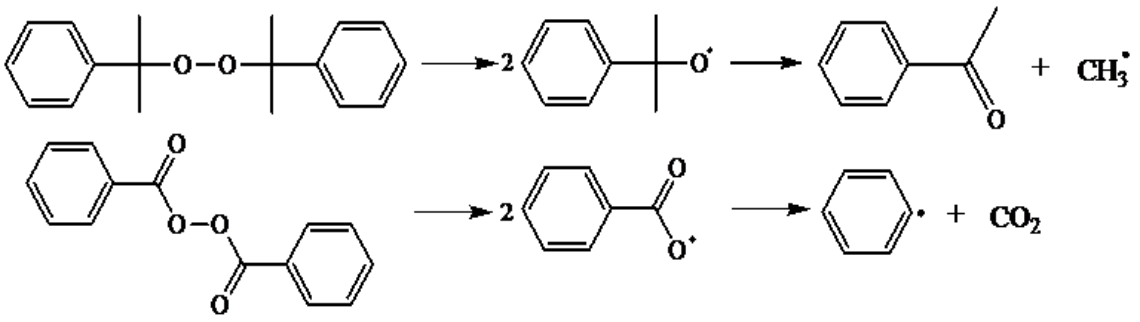
One of the important advantages of peroxide cures over sulphur cures is their ability to activate completely saturated polymers. Sulphur cure formulations require C=C unsaturation to generate a covalent network of sulfidic cross-links. Therefore, materials such as polyethylene and ethylene-propylene rubber cannot be cross-linked by sulphur, but are amenable to curing by the action of peroxides.[11,12]

Other cross-linking technologies have been developed solely for use on specific polymers. These include phenolic resin cures, benzoquinone systems, and metal oxide cures. However, in the case of phenolic and benzoquinone cures, the base polymer must contain allylic functionality to support cross-linking.[13,14] Metal oxides require allylic halogen in the polymer backbone to operate successfully as a curative.[4] As a result of their lack of general application, these cures have received relatively less attention when compared to the more widespread sulphur and peroxide cure systems.

1.3 Peroxide Cross-linking of Polymers

Peroxide cures function through the combination and addition reactions of free radical intermediates. Peroxides containing a labile O-O bond (BDE ~ 150 kJ/mol) usually serve as the source of free radicals, initiating curing by homolytic cleavage of the oxygen-oxygen bond to create alkoxyl radicals as their primary decomposition product. Unlike radical polymerizations that operate at relatively mild

temperatures, rubber mixing generates sufficient heat to raise compound temperatures above 100°C. Although several peroxides are commercially available, their selection is based on the initiator half-life at the processing temperature of the polymer. Examples of widely-used peroxide initiators (half-life, temp.) are dicumyl peroxide (9.2 mins, 150°C), di-*tert*-butyl peroxide (14mins, 150°C), 1,1-di(*tert*-butylperoxy)cyclohexane (18 mins, 150°C).[15]



Scheme 1.1: Decomposition and β-scission of dicumyl peroxide and dibenzoyl peroxide

Another advantage of peroxide initiators is their ability to generate oxygen-centered radicals (Scheme 1.1) that are relatively reactive toward hydrogen atom abstraction from saturated and unsaturated substrates.[16] Efficiency in hydrogen atom transfer is important to peroxide cure chemistry, since this is the means by which a polymer is activated to yield macro-radical intermediates that lead to cross-linking. Note that β-scission of alkoxyl radicals to yield ketone plus alkyl radical competes with hydrogen atom abstraction. Dicumyl peroxide, for instance, yields cumyloxyl radicals which further fragment to acetophenone and methyl radicals. Baignee et al. reported an increase in acetophenone concentration with temperature when cumyloxy radicals were generated in cumene,[17] suggesting that the activation energy for radical scission is greater than that for hydrogen atom transfer. It should be noted that benzoyloxyl radicals fragment more readily than the oxygen-centred radicals derived from dialkyl or diaryl peroxides, giving a phenyl radical and carbon dioxide.

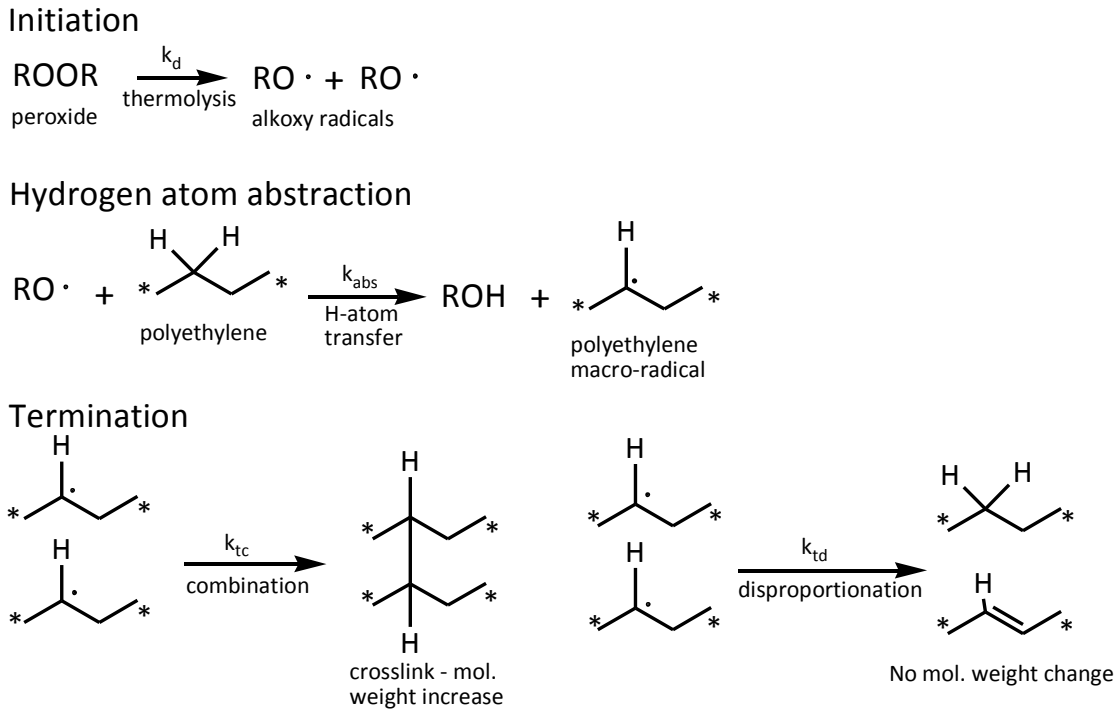
While alkoxyl and alkyl radicals are capable of both hydrogen atom transfer and addition to C=C bonds, they have markedly different preferences, with oxygen-centred radicals preferring abstraction and alkyl radicals preferring olefin addition.[15] For example, the rate constant for methyl radical addition to styrene is three orders of magnitude greater than that of hydrogen abstraction from 2,2,4-trimethyl pentane.[18]

Table 1.1: Bond strength of various types of C-H bonds[10]

Type of C-H bond	C-H bond strength (kJ/mol)
primary	435
secondary	405
tertiary	380
allylic	368
benzylic	368
phenyl	468

The yield of hydrogen atom transfer is affected not only by the properties of the abstracting radical, but also the structure of the hydrogen donor. The strength of the C-H bond in question is relevant when assessing the ease with which the hydrogen atom can be removed (Table 1.1). For example, resonance stabilization of allylic and benzylic radicals makes these positions better hydrogen donors than corresponding alkyl sites. Although the thermodynamics of hydrogen transfer often dominate reactivity, steric effects can also be important, particularly in polyisobutylene activation, in which steric encumberance by neighbouring quaternary carbons inhibits the reactivity of secondary sites along the polymer backbone.

While hydrogen atom abstraction from the polymer gives the macro-radicals needed to affect cross-linking, it is radical termination by combination that generates the desired covalent bond. Bimolecular termination of two radicals occurs at the diffusion limit of reaction velocity, with rate constants on the order of 10^9 $M^{-1}S^{-1}$.[16] Termination by radical combination (k_{tc}, Scheme 1.2) yields the desired covalent cross-link between polymer chain segments, while disproportionation (k_{td}, Scheme 1.2) has no direct effect on polymer molecular weight.



Scheme 1.2: Simplified mechanism for the peroxide-curing of polyethylene

In general, the radical species must have an α-hydrogen in order to terminate through disproportionation. For those radicals capable of both termination modes, clearly each has its preferred mode of termination. Table 1.2 lists the ratios of the rates of disproportionation to combination for some species. Of note is the propensity of the allylic radicals to terminate exclusively through combination, suggesting the presence of unsaturation aids radical-mediated curing of this class of materials. Benzylic and primary alkyl radicals also prefer combination but not exclusively.

Table 1.2: Ratio of disproportionation to combination of radicals in solution[19]

Radicals	k_{td}/k_{tc}
$2CH_3\dot{C}H_2$	0.15[a]
$2(CH_3)_2\dot{C}H$	1.2[a]
$2(CH_3)_3\dot{C}$	7.2[a]
$2CH_2=CH\dot{C}(CH_3)_2$	~0[b]
$2C_6H_5\dot{C}HCH_3$	0.14[c]

a.30°C in n-pentane; b.49°C in o-dichlorobenzene; c.105°C in benzene.

Polyethylene (PE), which mostly consists of secondary carbons, is cross-linked in the presence of free radical initiators because of the tendency of the secondary radicals to combine.[2] Ethylene propylene rubber (EPR), containing 50-60 mol% of ethylene units has been shown to undergo cross-linking in the presence of peroxide. It has been reported that both cross-linking due to ethylene units and scission due to propylene units takes place simultaneously but due to the presence of excess ethylene units, cross-linking predominates.[11]

Some commercially available polymers contain low amounts of unsaturation to make them responsive to peroxide cure formulations. For example, a terpolymer of ethylene, propylene and 1- 2mol% of ethylidene norbornene yields the commodity elastomer, EPDM. The ter-monomer content in this elastomer is important to peroxide cures as it provides allylic sites for hydrogen abstraction, thereby improving macro-radical yields and increasing cross-link density.[10] Similarly, hydrogenated nitrile-butadiene rubber (HNBR) contains ~5% of the residual C=C within unconverted butadiene-mers can cross-linked by peroxide formulations.[20] Completely unsaturated elastomers such as polyisoprene[21] and polybutadiene[22] cross-link extensively under the action of radical generating techniques.

However, not all polymers are peroxide-curable, as some undergo chain scission in opposition to cross-linking. For example, polypropylene degrades in the presence of 2,2-dimethyl-2,5-(*tert*-butylperoxy)hexane at 200°C.[23] If the yield of macro-radical scission exceeds that of macro-radical combination, the net effect of peroxide modification is to decrease molecular weight. Other degradative mechanisms can prevent polymers from responding well to peroxide cures. For example, polyvinyl chloride undergoes dehydrohalogenation side-reactions that are believed to inhibit peroxide vulcanization.[24]

The mechanism by which unsaturated elastomers are cross-linked by peroxides remains unclear. Ostromislensky, who first suggested the use of organic peroxides for vulcanization of natural rubber, proposed that cross-linking takes place through allylic hydrogen abstraction, followed by allyl radical combination. This would yield cross-links without consuming olefinic functionality. Subsequent model compound studies by Farmer and coworkers confirmed that hydrogen abstraction plus macro-radical coupling is predominant, with 85% of the unsaturation in the starting materials being found in reaction products.[25,26,27] However, the apparent consumption of some C=C bonds suggested other cross-linking mechanisms involving unsaturation. Interestingly, their work included reactions of di-*tert*-butyl peroxide with cyclohexene and hept-1-ene separately. While the cyclohexene experiments yielded di-, tri-, and tetra-mers by allyl radical coupling, the main products of hept-1-ene reactions were saturated oligomers, although some allylic coupling was also reported.

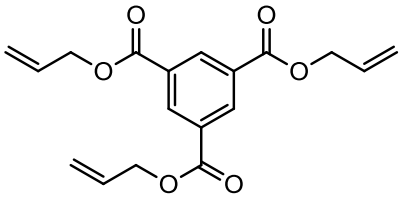
These results offered early insight into potential C=C oligomerization in some peroxide curing processes. In 1963, Van Der Hoff compared the cross-link densities generated by polyisoprene and polybutadiene.[28] At a given peroxide concentration, cross-linking in polybutadiene was found to be at least 10 times more efficient than in polyisoprene. The author suggested that the difference in peroxide cure efficiency is due to the kinetic chain length associated with a radical oligomerization process in the polybutadiene

system that gave multiple crosslinks from each initiator-derived radical. However, this type of chain reaction process has not been reported for other polymers, leaving stoichiometric cures involving macroradical coupling to most elastomers of commercial interest.

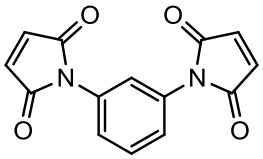
1.4 Coagent Assisted Cross-linking of Polymers

Coagents are poly-functional monomers that are added to peroxide cure formulations to boost the extent of cross-linking. As discussed above, peroxide-only cures are largely stoichiometric processes that yield a maximum one cross-link per molecule of initiator. Therefore, cure yields generally scale with peroxide loading, and tighter network densities are generated at a cost of higher initiator concentrations. The inclusion of a coagent can, in some cases, provide an alternate cure mechanism that yields cross-links without consuming macro-radical intermediates, thereby allowing higher cure extents to be reached at a given peroxide loading.

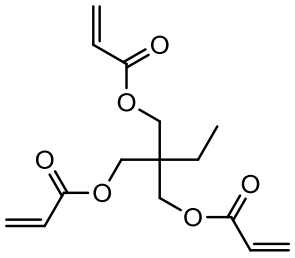
Several classes of coagents are available, differing in terms of the amount (di-functional, tri-functional, poly-functional) and type of C=C functionality (acrylic,[29,30] styrenic, maleimido,[5,] vinylic,[31] allylic[32]). Examples of commonly used coagents are illustrated in Figure 1.2. Most coagents are neutral compounds, but metallic salts such as zinc diacrylate and zinc dimethacrylate can be used to enhance cross-link yields while introducing ion-pairs to the thermoset article.[33] Polymeric coagents like 1,2-polybutadiene are also less popular, but they have been shown to be effective on polyethylene cross-linking systems.[31]



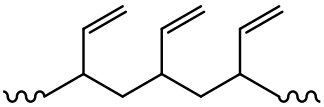
Triallyl trimesate (TATM)



N,N' -m-phenylenedimaleimide (HVA-2)



Trimethylolpropane triacrylate (TMPTA)

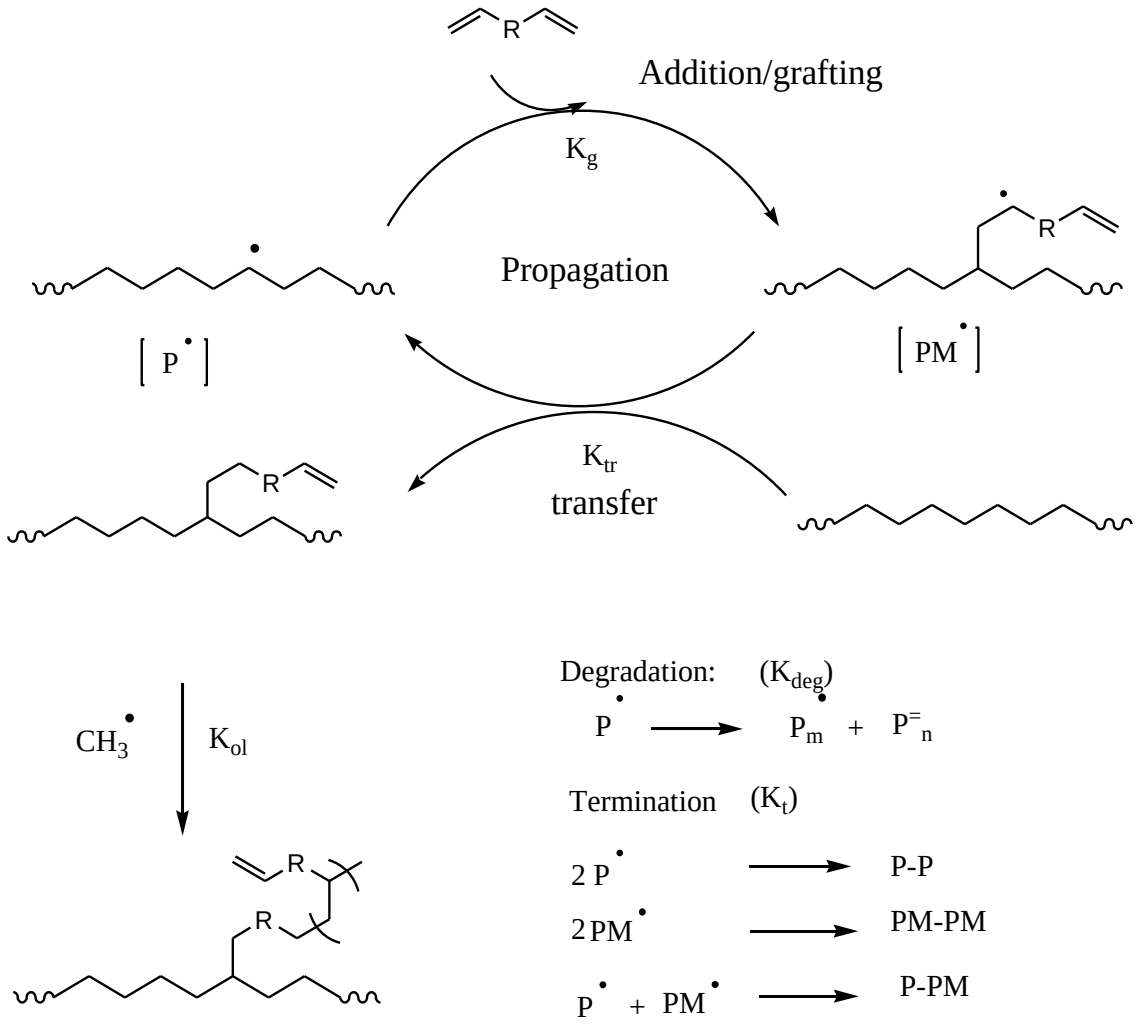


1,2 - polybutadiene

Figure 1.2: Examples of coagents used in peroxide cure formulations

The consumption of coagent unsaturation during the curing process has been well documented,[29] suggesting that additional cross-link density is generated by C-H bond addition by the polymer to the C=C functionality provided by the coagent. This is formally a graft-modification process analogous to the addition of polyolefins to maleic anhydride and vinylsilanes, which yield pendant succinyl and alkylsilane groups, respectively. In the context of polyolefin cross-linking, repeated C-H addition of the polymer to the multiple C=C groups in the coagent or coagent oligomer gives the required covalent cross-links. If this grafting process has a significant kinetic chain length, then a covalent network is generated by a non-stoichometric process wherein a single initiator-derived radical can produce several cross-links.[15]

Although monomers used for grafting purposes usually are mono-functional, the mechanism of grafting can be extended to radical-mediated coagent cross-linking of polymers. Scheme 1.3 illustrates the mechanism of coagent activity in a peroxide curing system. When the grafting cycle is repeated for a multifunctional molecule, it generates cross-links.



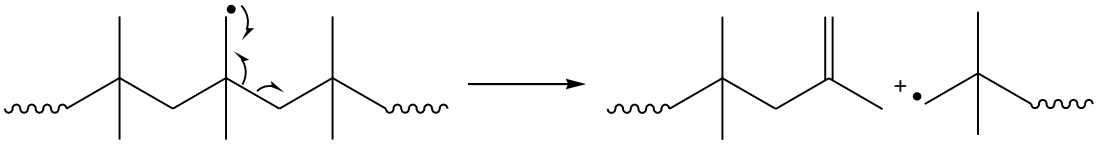
Scheme 1.3: Generic mechanism of coagent assisted peroxide cross-linking of polymers

The most widely encountered side reaction during coagent-assisted cross-linking is oligomerization. Acrylates and methacrylates are widely known to undergo homo-polymerization at moderate temperatures. However, typical cure temperatures are well above 150°C, which can decrease coagent oligomerization because of ceiling temperature effects. While oligomerization is a major side reaction, it is not the only pathway leading to the low efficiency of cures. It has been reported that triallyl cyanurate undergoes intramolecular cyclization, hence lowering the cross-linking efficiency.[34]

1.5 Peroxide cross-linking of isobutylene-rich elastomers:

Polyisobutylene (PIB) is valued for its chemical resistance, vibration dampening characteristics, and superior air impermeability. The latter is attributed to its relatively high density (0.917 g/cm^3) compared to other elastomeric materials.[35] PIB also provides exceptional resistance to free radical oxidation, presumably due to the high C-H bond dissociation energy of pendant methyl groups, which disfavours hydrogen atom abstraction from the polymer. Steric hindrance is thought to limit the potential for hydrogen atom abstraction from secondary positions along the polymer chain, leaving primary methyl functionality as the principal hydrogen atom donor.

Unlike other saturated elastomers such as poly(ethylene-co-propylene), PIB does not undergo free radical cross-linking, but degrades when heated with peroxides at conventional curing temperatures.[36] This is due to macro-radical fragmentation, which lowers the polymer's molecular weight to a greater degree than radical combination increases it. The β-scission of primary alkyl macro-radicals is believed to result in PIB degradation, as is illustrated in Scheme 1.4.



Scheme 1.4: Radical-mediated degradation in polyisobutylene

Poly(isobutylene-co-isoprene), also known as butyl rubber and IIR, is a random copolymer prepared by cationic copolymerization of isobutylene with 1-2 mol% isoprene. The chemical structure of IIR is very similar to PIB, except for the randomly distributed isoprene mers that serve as reactive sites for vulcanization (Figure 1.3). IIR is widely used in tire inner tube applications, which utilize conventional sulfur cure formulations for compound cross-linking. In the context of peroxide curing, isoprene mers provide allylic hydrogen that engage more readily in atom transfer to alkoxyl radicals than the primary and secondary sites elsewhere in the polymer chain. As noted above, allylic radicals terminate

exclusively by combination, so their formation in IIR is expected to mitigate chain scission when the elastomer is treated with peroxides. Loan demonstrated a direct correlation between the isoprene content of IIR and changes in molecular weight brought about by peroxides. He found that in order for the butyl rubber to overcome the degradation and subsequently cross-link, it must contain a minimum of 3 mol% isoprene units.[37] However, these isoprene levels are insufficient to support the cross-link densities required of most engineering applications.[38]

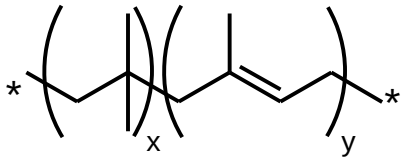


Figure 1.3: Structure of poly(isobutylene-co-isoprene) or butyl rubber

As discussed in earlier sections, bismaleimide coagents are commonly used in commercial practice, and they have been applied to butyl rubber formulations. In 1999, Sudo et al. cured butyl rubber with an isoprene content in the range of 0.5 to 2.5 mol% using 3.5 parts by weight organic peroxide and 0.3 to 4% by weight of bismaleimide based compounds.[39] In 2005, Resendes et al. increased the content of isoprene in butyl rubber to 7.5 mol%, using 0.1mol% of divinyl benzene to offset the molecular weight loss incurred when high isoprene levels are used in cationic polymerizations.[40] Their formulations contained 4 parts by weight dicumyl peroxide and 2.5 parts by weight N,N'-m-phenylene dimaleimide, and provided superior cure yields those generated by Sudo et al. Similar results were reported by Knight et al. on IIR containing 8 mol% isoprene, wherein 10 parts by weight peroxide and 4-6 parts by weight bismaleimide coagent were employed.[41] Although these butyl rubber compositions have better peroxide cure performance, they require very high isoprene content to achieve such results. This may pose a problem, as residual C=C in elastomers generally compromises long-term aging characteristics, due to its susceptibility to oxidation and ozonolysis.[42]

A different approach was explored by Oxley and Wilson in 1969, involving isobutylene-rich terpolymers containing isoprene and divinyl benzene.[43] The cationic polymerization of these monomers was carried out in methyl chloride with $AlCl_3$ as catalyst, and gave 85 wt% gel, owing to cross-linking through divinylbenzene during the polymerization process. The presence of residual styrenic functionality in these polymers was not reported, but the ability of these materials to cure in the presence of dicumyl peroxide has been demonstrated through rheological measurements.

This multiple comonomer strategy was continued by Resendes et al., who produced a gel-free butyl rubber containing 82.8% isobutylene, 15.7% p-methylstyrene and 1.49% isoprene.[44] This terpolymer did not cure under the action of organic peroxides alone, but required bismaleimide coagent to produce a thermoset article. Hence, their formulations contained 4 parts by weight dicumyl peroxide and 2.5 parts by weight N,N'-m-phenylene dimaleimide.

1.6 Derivatization of Halogenated butyl rubber

Halogenated poly(isobutylene-co-isoprene), known as BIIR for brominated grades and CIIR for chlorinated grades, are produced commercially for the tire inner liner market. IIR halogenation is carried out in hexanes solution using elemental chlorine or bromine, and proceeds through an ionic substitution mechanism. In the case of BIIR, three isomers can be generated (Figure 1.4) with the exo-methylene bromide being the kinetically favoured bromination product. At elevated temperatures, this exo-methylene bromide isomer will rearrange to the more thermodynamically stable E,Z-BrMe isomers, and this can be accompanied by dehydrobromination to give conjugated dienes.[45]

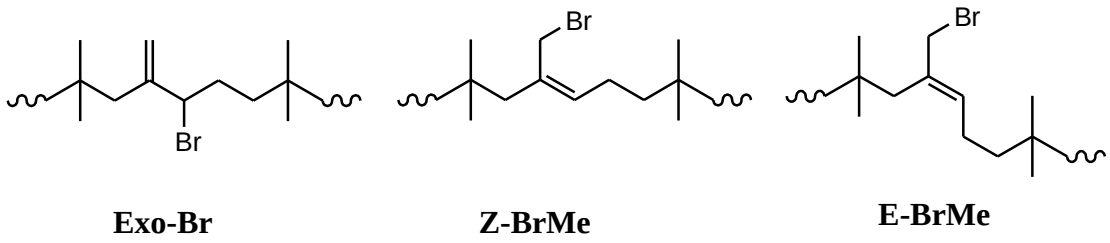


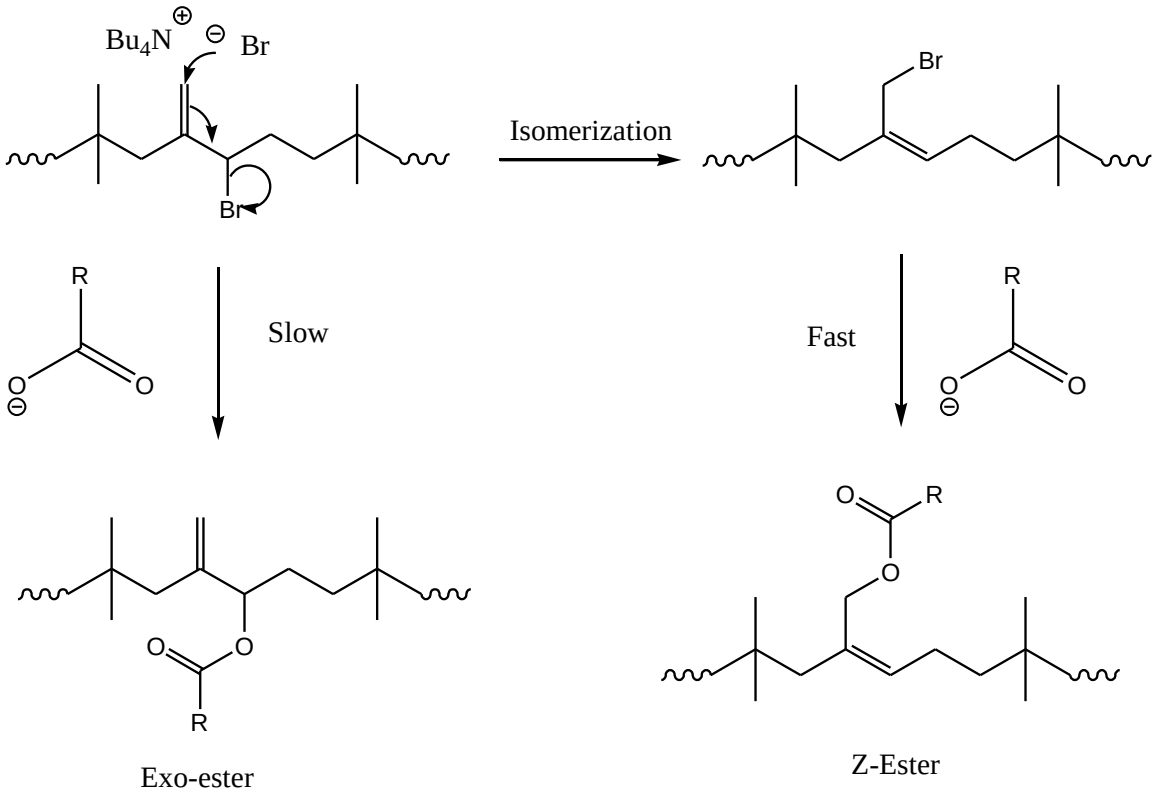
Figure 1.4: Isomeric structures of allylic bromides in BIIR

Due to the polarised nature of carbon–bromine bond, allylic bromides function are good σ-bond electrophiles, undergoing a range of bimolecular nucleophilic substitution reactions[46] at rates 10 – 100 times greater than aliphatic halides.[47] This has been exploited to prepare a wide range of IIR-based materials through nucleophilic displacement of bromide from BIIR. For example, Williamson ether synthesis conditions have been adapted to use potassium salts of monohydroxy poly(ethylene glycol)to displace bromide from BIIR, yielding butyl rubber with grafted chains of polyethylene glycol.[48] Furthermore, a moisture curable derivative of BIIR has been prepared by halide displacement using 3-aminopropyltriethoxysilane.[49]

Nitrogen based nucleophiles such as N,N-dimethyloctylamine (3°), N-methyloctadecyl amine (2°) and octylamine (1°) were reacted with BIIR in the solid state at high temperature. While the tertiary and secondary amines yielded mono N-alkylation products, the primary amine engaged in bis-alkylation, leading to a cross-linked thermoset.[50] In all cases, the reversibility of N-alkylation limited reaction extents, and excess nucleophile was required to achieve complete allyic halide conversion. The mono-alkylation product of tertiary amines yields ionomer derivatives that provide heightened strength owing to a network of ion-pair aggregates.[51] By analogy, phosphonium-based ionomers were made by reaction of triphenylphosphine and BIIR. Although, these P-alkylation products were more stable than their corresponding quaternary ammonium salts, phosphines containing additional chemical functionality are not commercially available, limiting the scope of this technology to PPh_3.

Thioether derivatives of IIR were prepared from BIIR and CIIR using dodecanethiol in a base-mediated process.[52] A difference in the reactivity between CIIR and BIIR was also reported with CIIR proving to be limited in its capabilities of supporting a nucleophilic substitution by thiolates. While the ether derivatives of BIIR were successfully prepared from aliphatic and aromatic alcohols, the reaction needed severe conditions and suffered from low yields as well.[53] Aliphatic alkoxide ions were formed *in situ* and reacted with BIIR directly whereas aryloxy ions required quaternary ammonium salts in order to participate in the reaction.

The use of charged nucleophiles for BIIR modification chemistry poses several challenges, since they are insoluble in non-polar elastomers and the solvents in which these polymers readily dissolve. This is true of carboxylate nucleophiles, which react with the allylic bromide functionality within BIIR irreversibly and to very high yields. These characteristics, coupled with the availability of a wide range of functional and polymeric carboxylate nucleophiles, makes BIIR esterification an attractive synthetic approach. However, phase transfer catalysis (PTC) is required to render carboxylate nucleophiles soluble in BIIR and its solutions, as has been demonstrated by Guillen et al.[54] Among the phase transfer catalysts used for these studies, quaternary ammonium salts were reported to give the highest yield. The success of this approach provided a simple means of introducing pendant ester functionality ranging from small molecules to graft copolymers.[55]



Scheme 1.5: Isomerization and esterification of BIIR

In addition to generating soluble and nucleophilic carboxylate anions, quaternary ammonium bromide salts alter the microstructure of BIIR. Commercially available material contains 95% exo-bromide and 5% E-BrMe functionality. However, it is known that the exo-bromide is the kinetically favoured product of bromination, and it will isomerize to more thermodynamically stable E,Z-BrMe isomers. This reaction can be brought about thermally, but is also catalyzed by tetrabutylammonium bromide (TBAB) under mild conditions (Scheme 1.5).[56] Interestingly, the reactivity of E,Z-BrMe isomers is far greater than Exo-Br, so isomerisation of the starting material greatly improves nucleophilic substitution rates. This is of particular value when unstable functional groups are involved in the esterification process, necessitating the use of short reaction times.

Xiao et al. used phase-transfer catalyzed esterifications of BIIR in dilute toluene solution to prepare acrylate and vinylbenzoate derivatives that cured readily when activated by dialkyl peroxide.[57] These

multi-functional macro-monomers generate cross-linked thermosets by radical oligomerization of pendant functionality, as opposed to modifying the polymer backbone. As a result, these materials peroxide cure to high extent, as indicated by large increases in the polymer's complex modulus. Since these derivatives require only low concentrations of peroxide to reach this state of cure, the resulting thermosets are expected to be clean relative to coagent-assisted peroxide cures, and sulfur-based vulcanization systems. As a result, this demonstration of IIR-derived macromonomer structure and properties is an important precedent for many of the experiments described in the current work.

1.7 Research Objectives:

A longstanding collaboration between the Parent group and the butyl rubber division of LANXESS Inc. has generated an improved understanding of BIIR chemistry, particularly with respect to the synthesis and properties of chemical derivatives. Interest in isobutylene-rich elastomers that are peroxide-curable was generated with the patent filing of Resendes et al. in 2005, which claimed high isoprene grades of IIR could be cured to high extent when compounded with bismaleimide coagents. The research described in this thesis had several objectives related to this area of polymer chemistry.

1. Determine the mechanisms through which maleimides enhance the efficacy of peroxide cure formulations when applied to saturated and unsaturated polymers.
2. Determine the mechanism of bismaleimide cure formulations acting on high isoprene grades of butyl rubber.
3. Design and evaluate alternate isobutylene-rich elastomers that cure more effectively than IIR in maleimide cure formulations.
4. Characterize the cure reactivity and auto-initiation stability of macro-monomer derivatives of IIR that bear acrylate, styrenic, maleimide, and other C=C functional groups.

5. Prepare and evaluate macro-monomer derivatives of IIR that cure to high extent when activated by peroxide alone, and bear additional functionality that is capable of modifying the physical and/or chemical properties of the elastomer.

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Chapter 2 : C–H bond addition and copolymerization reactions of N-arylmaleimides: Fundamentals of coagent-assisted polymer cross-linking

2.1 Introduction:

Cross-linking of elastomers and semi-crystalline polymers generates thermoset derivatives whose mechanical and thermal properties are significantly better than their parent materials.[1] For saturated polymers that are not amenable to sulphur cures, and in cases where cross-link stability is valued over dynamic properties, free radical chemistry is generally preferred.[2] These reactions proceed through an open sequence of hydrogen atom abstraction from the polymer by peroxide-derived radicals, and subsequent macroradical combination to generate a carbon-carbon cross-link. As such, the cross-link yield of peroxide-only cures cannot exceed the peroxide loading, and can be significantly lower depending upon the abstraction efficiency of the initiator and the extent of macroradical termination by disproportionation.

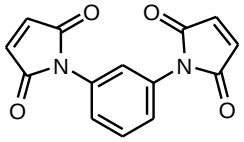
Polymers containing C=C unsaturation are more amenable to peroxide curing, owing to the heightened reactivity of allylic C-H bond to hydrogen atom abstraction and, to some extent, to cross-linking through C=C oligomerization. For example, 1,2-polybutadiene reportedly provides multiple cross-links per initiator radical, presumably by macroradical addition to the residual olefinic functionality within the elastomer[3]. Steric hindrance disfavours this route for other diene-based polymers such as 1,4-polybutadiene and polyisoprene[4], resulting in lower cross-link yields than those recorded for elastomers containing pendant vinyl functionality.[5,6]

To improve the cross-link density generated by a peroxide cure, small molecules containing multiple allylic, acrylic, or maleimide groups are frequently employed (Scheme 2.1). Activation of the C=C

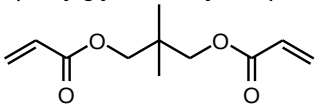
functionality within these coagents can produce cross-links through closed propagation sequences that do not consume radical intermediates. The faster these sequences proceed relative to macroradical termination, the higher the cross-link density that can be achieved at a given peroxide loading. Acrylate and malemide-based systems, commonly referred to as Type 1 coagents, are kinetically reactive, requiring small amounts of initiator to boost the state of peroxide cures.[7] This can lead to scorch safety problems[8], which in many cases leads to the use of Type II coagents, whose allylic functionality is less reactive, generally providing scorch protection at the expense of higher peroxide requirements. [9],[10]

Despite the widespread use of coagent technology, commercial development has outpaced studies of its fundamental chemistry. This work is concerned with free radical additions of maleimide-based coagents to saturated and unsaturated polymers, with the objective being an improved understanding of why maleimide-based systems are so effective, and why their performance varies amongst different polymer structures. Insight into these issues is gained through rheological studies of polymer cross-linking dynamics and yields, and detailed characterizations of model compound reaction products.

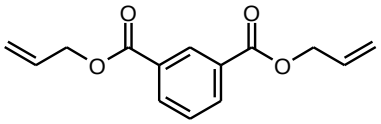
N,N'-m-phenylenedimaleimide (BMI)



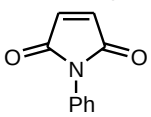
Neopentylglycol diacrylate (NDA)



Diallylisophthalate (DAIP)



N-phenylmaleimide (NPM)



Scheme 2.1 Cross-linking coagents of interest

2.2 Experimental:

Materials

cis-1,4-Polybutadiene (PBD, M_w=200 kg/mol), polyethylene oxide (PEO, M_w=5,000 kg/mol), polyisobutylene (PIB, M_w=400 kg/mol, and polyisoprene (PIP, M_w=800 kg/mol) were used as received from Scientific Polymer Products. Linear low-density polyethylene (LLDPE, 6 mol% hexane), butyl rubber (IIR, 2.8 mol% isoprene, RB-301, LANXESS) were used as received. Dicumyl peroxide (DCP, 99%), cyclooctane (99%), *cis*-cyclooctene (95%), N-phenylmaleimide (NPM, 97%), 1,2,4-trichlorobenzene (99%), N,N'-*m*-phenylene dimaleimide (BMI, 97%), and neopentyl glycol diacrylate (NDA, 99%) were used as received from Sigma-Aldrich. Diallyl isophthalate (DAIP, 98%) was used as received from Tokyo Chemical Company.

Cure Rheology

Polybutadiene, polyisoprene, polyisobutylene and butyl rubber (5g) were each coated with the required amount of DCP from a stock solution in acetone and dried. Dried rubber samples were then passed through a two roll mill several times. Coagents were incorporated into the rubber samples during passes through the two roll mill. The mixed samples were then cured in the melt sealed cavity of a parallel plate rheometer (Alpha Technologies APA 2000 rheometer, biconical plates) at 160°C, 1Hz and 3° arc. LLDPE and PEO samples (5 g) were each tumble mixed after the required amount of DCP and coagents were added as acetone solution. Dried LLDPE samples were cured as described above.

N-phenylmaleimide grafting to cyclooctane

Cyclooctane (9 g, 80 mmol) combined with the required amounts of DCP and NPM in a 25 mL glass tube. The vessel was immersed in an oil bath at 160°C under constant magnetic stirring. Unreacted starting

materials were removed by Kugelrohr distillation (0.03 bar; 100°C). The residue was washed with isopropanol to isolate non-oligomeric compounds, which were then subjected to gas chromatography using a Hewlett-Packard 5890 series II instrument equipped with a flame ionization detector (1µL injection volume, helium as carrier gas, Si column, 50°- 290°C). The column was heated from 50° - 200°C at the rate of 10°C/min and held at 200°C for 5 min followed by heating to 290°C at the rate of 30°C/min and held at that temperature for 15 min.

Synthesis of *N*-Phenylcyclooctylsuccinimide

Cyclooctane (9 g, 80 mmol) was combined with the required amount of DCP (0.009 g, 0.03 mmol) and NPM (0.0225 g, 0.13 mmol) and sealed within a 25 mL glass tube before being immersed in a silicone oil bath at 160°C under constant magnetic stirring. Unconverted reagents were removed by Kugelrohr distillation (0.03 bar; 100°C), and the residue was washed with isopropanol to isolate non-oligomeric compounds. The isopropanol solution was fractionated by semi-preparative, normal-phase, high pressure liquid chromatography (HPLC) using a Waters Model 400 instrument equipped with UV-vis and refractive index detectors (isopropanol as eluent, Supelcosil PLC-Si column). MS analysis: required mass for $C_{18}H_{23}NO_2$ is 285.1742 m/e; found 285.1729 m/e (TOF MS EI+). Melting point: 112 - 116°C. ^{1}H NMR ($CDCl_3$) : δ 7.46 (tt, 2H), δ 7.38 (tt,1H), δ 7.26 (dd, 2H), δ 3.02 (ddd, 1H), δ2.89 (dd, 1H), δ2.65 (dd, 1H), δ2.43 (dd, 1H), δ1.4 -1.8 (m, 14H).

Synthesis of poly(N-phenylmaleimide)

N-phenylmaleimide (0.09 g, 0.52 mmol) was mixed with DCP (0.009 g, 0.03 mmol) in 1,2,4- trichloro benzene solution (9 g) and sealed within a 25 mL glass tube before being immersed in a silicone oil bath at 160°C under constant magnetic stirring. Poly(N-phenylmaleimde) was isolated by precipitating the

mixture in methanol. Polymer was further purified by dissolution/precipitation technique in acetone/methanol and dried under vacuum. ^{1}H NMR ($CDCl_3$) : δ 7.0-7.5 (Ar, 5H), δ 3.0-5.0 (m, 2H).

Copolymerization of cyclooctene and N-phenyl maleimide

Cis-cyclooctene (9g, 81mmol) was mixed with the required amount of DCP and N-phenylmaleimide and sealed within a 25mL glass tube. The reactor vessel was immersed in an oil bath at 160°C under constant magnetic stirring. The copolymer was isolated through successive dissolution/precipitation in dichloromethane/hexanes. ^{1}H NMR ($CDCl_3$) : δ 7.46 (m, 1H), δ 7.38 (m,1H), δ 7.26 (m, 2H), δ2.61 (m, 2H), δ2.19(m, 1H), δ1.4 -1.8 (m, 14H).

Instrumentation and Analysis

^{1}H NMR was recorded with a Bruker 600MHz instrument using $CDCl_3$. High resolution mass spectroscopy was conducted using a Waters/Micromass GCT- TOF mass spectrometer operating under electron impact mode. Differential Scanning Calorimetry (DSC) analysis was conducted with three heating-cooling cycles (at 10 °C/min) using a DSCQ100 apparatus (TA Instruments) with nitrogen purge. Elemental analysis was carried out at Canadian Microanalytical Services.

2.3. Results and Discussion

We will show that the radical chemistry that underlies a maleimide-assisted cure depends on whether the polymer is completely saturated, or contains some amount of C=C unsaturation. We start with saturated polymers, particularly LLDPE, before considering the cure chemistry of unsaturated materials such as cis-polybutadiene.

2.3.1 Cross-linking of saturated polymers

Time-resolved measurements of dynamic storage modulus (G') recorded at fixed temperature, strain and frequency are standard measures of cross-link density and, by extension, cure dynamics and yields.[11] The data plotted in Figure 2.1a show that a dicumylperoxide loading of 3.6 μmole/g raised the modulus of LLDPE from 11 kPa to 27 kPa over 60 minutes at 160°C. The dynamics of these simple cures are governed by the relatively slow rate of peroxide thermolysis. Given the 5 min half-life of DCP at 160°C, this reaction was essentially complete after 30 minutes.

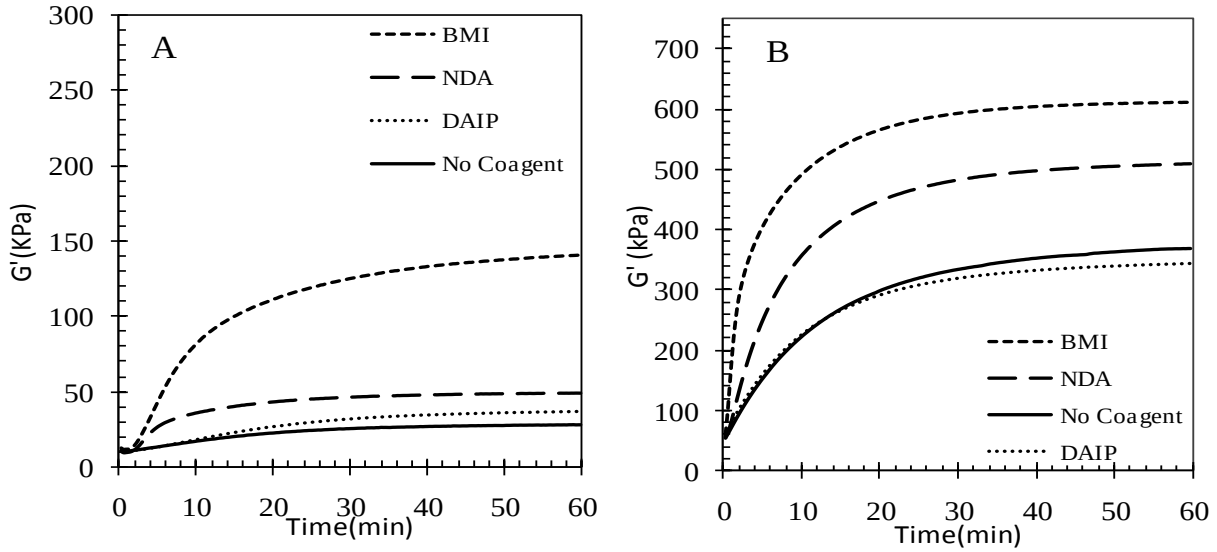


Figure 2.1: Dynamics of coagent-assisted cross-linking (A. LLDPE; B. PBD; 160°C; 1 Hz, 3° arc; [DCP] = 3.6 μmol/g; [coagent] = 0.72 mmol/g)

Since peroxide-only formulations cure LLDPE essentially through macroradical combination, cross-link yields cannot exceed the amount of initiator. However, provision of a coagent provides an opportunity to increase the cross-link density that can be achieved at a given peroxide loading. The data illustrated in Figure 2.1A show that allylic and acrylic-based coagents are relatively ineffective on LLDPE. On the other hand, the bismaleimide coagent, BMI, improved cross-link densities dramatically, increasing the final storage modulus five-fold over the DCP-only system. This is consistent with studies of

poly(ethylene-co-propylene) crosslinking by Alvarez Grima, whose rheological data showed that a bis-maleimide coagent produced torque values of more than twice those provided by acrylic and allylic coagents.[12]

The superiority of BMI over diacrylate and diallyl coagents extends over a range of saturated polymers. Table 2.1 lists the change in storage modulus ($\Delta G' = G'_{final} - G'_{initial}$) for cure formulations applied to LLDPE, polyethyleneoxide (PEO) and polyisobutylene (PIB). Heating PEO with 3.6 µmole of DCP per gram of polymer to 160°C decreased the material's storage modulus by 372 kPa, owing to severe macroradical fragmentation. Neither DAIP nor NDA was capable of preventing PEO chain scission, but BMI produced a net gain in storage modulus of 284 kPa. This is a remarkable result, in that 0.72 mmole BMI per gram of polymer transformed a material that incurs substantial degradation into one that cures to a high extent. PIB also degrades under the action of DCP, yet in this case no coagent could produce a cured article – only the extent of chain scission could be mitigated by BMI, DAIP or NDA.

Table 2.1: $\Delta G' = G'_{final} - G'_{initial}$ (kPa) recorded for peroxide cure formulations

	Saturated Polymers			Unsaturated Polymers		
Formulation	LLDPE	PEO	PIB	PBD	PIP	IIR
DCP	16	-372	-62	314	78	-34
DCP+BMI	128	284	-32	552	294	14
DCP+NDA	38	-248	-16	454	14	-26
DCP+DAIP	25	-239	-49	289	83	-17

[DCP] = 3.6 µmol/g; [Coagent] = 0.72 mmol/g; 160°C; 1 Hz; 3° arc.

The chemistry underlying coagent-assisted cures is difficult to determine from polymeric systems, owing to their low functional group content, and the insolubility of thermoset reaction products, which precludes solution NMR characterization. Therefore, detailed studies of model compound reaction products that can be isolated and characterized unambiguously are needed to gain insight into the

unique efficiency of maleimide-based coagents. We chose cyclooctane as a model for LLDPE based on its reasonably high boiling point, a lack of regio-isomers amongst its reaction products, and its relatively high reactivity toward hydrogen atom donation.[13] N-Phenylmaleimide (NPM) was used in the place of BMI due to its superior solubility in hydrocarbons, and to simplify product separation and analysis.

Heating a cyclooctane solution containing 28 μmol/g NPM to 160°C for 30 min had little effect, but the inclusion of 1.8 μmol/g DCP resulted in the complete consumption of monomer, as determined by ^{1}H NMR analysis. That a comparatively small amount of peroxide proved capable of converting all the NPM charged to the system is clear evidence of the reaction's chain character. The peroxide yield for this reaction, defined as the moles of converted monomer per mole of initiator-derived radicals, was 7.7 mol/mol. Since monomer concentrations declined to zero during our batch reactions, this peroxide yield represents the absolute minimum kinetic chain length for NPM conversion. Nonetheless, values as high as 16.1 mol/mol were recorded at high NPM concentrations – clear evidence of a radical chain process (Table 2.2).

Table 2.2 Radical addition of NPM to cyclooctane

NPM loading (μmol/g)	NPM conversion (%)	Peroxide Yield (mol/mol)	Single graft yield (% of NPM loading)	Multiply-grafted residue (% of NPM loading)	Cyclooctane : NPM in multiply-grafted residue
14	100	1.9	79	21	1:1.9
29	100	4.0	51	49	1:2.5
58	100	7.5	17	83	1:3.0
116	100	16.1	15	85	1:3.6

DCP = 3.6μmol/g; T=160°C; t=30 min.

Removal of residual cyclooctane by Kugelrohr distillation gave the crude product whose ^{1}H NMR spectrum is shown in Figure 2.2a. Fractionation of this crude mixture by HPLC isolated the 1:1 cyclooctane + NPM addition product, N-phenylcyclooctylsuccinimide (Figure 2.2b), from residual graft-

modified material, whose 1:1.9 cyclooctane:NPM composition (Figure 2.2c) was determined from aromatic and aliphatic ^{1}H NMR resonance integrations.

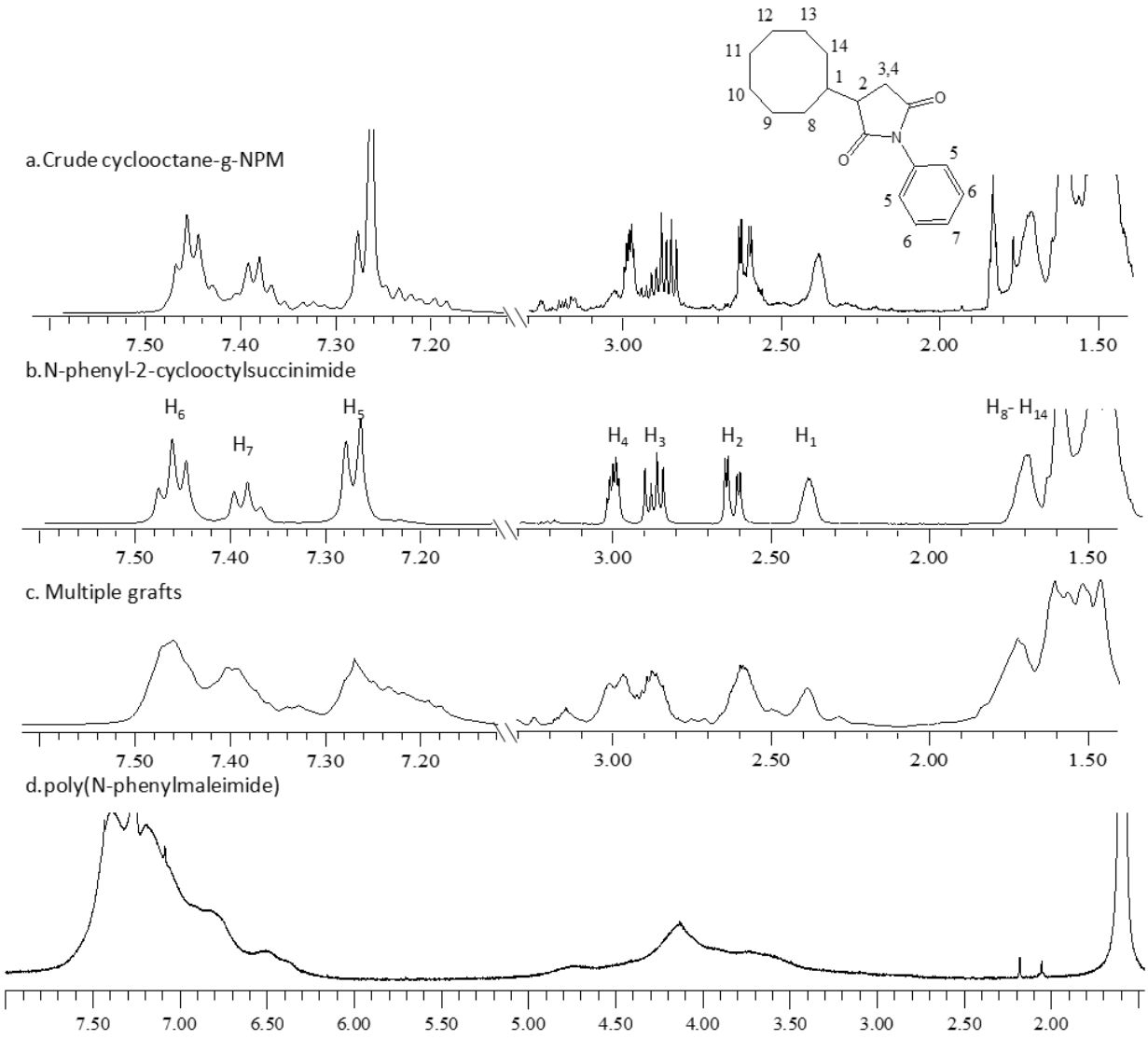
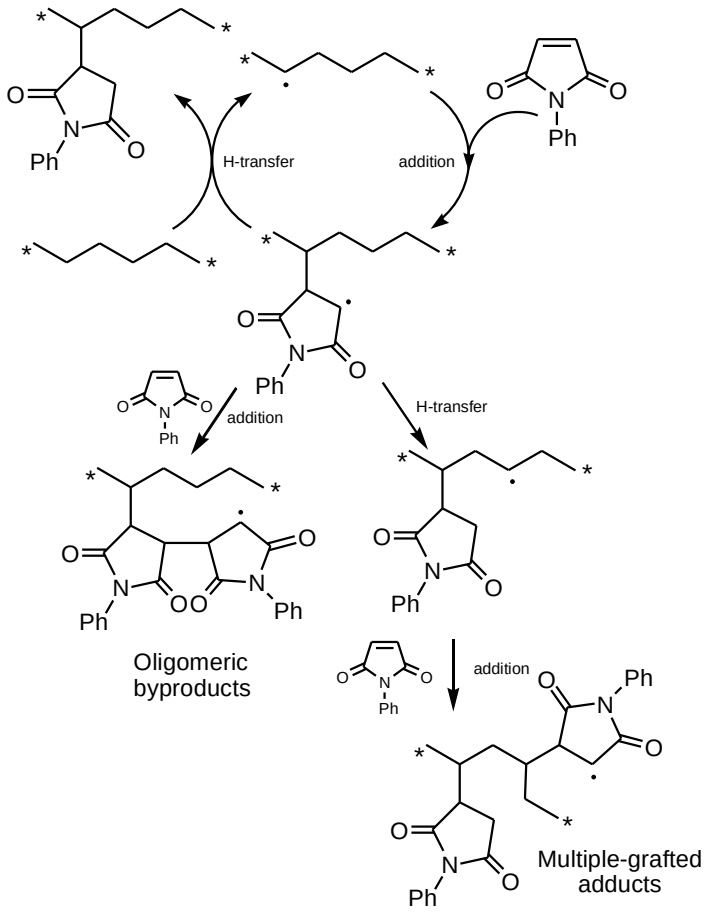


Figure 2.2: ^{1}H NMR spectra ($CDCl_3$) of (a) crude cyclooctane-g-NPM, (b) N-phenylcyclooctylsuccinimide, (c) multiply-grafted residue, (d) poly(NPM).

The 1:1 adduct, N-phenylcyclooctylsuccinimide, was produced by alkyl radical addition to NPM, followed by hydrogen atom abstraction by the resulting succinimidyl radical from the hydrocarbon (Scheme 2.2). The efficiency of this C-H bond addition can be dictated by either component of this propagation sequence. If maleimide addition to alkyl radicals is rate controlling, then reaction kinetics will be first-order in monomer. If the hydrogen atom transfer step is rate limiting, then a zero-order monomer

dependence is expected.[14] Lee and Russell studied the peroxide initiated reaction of 67 μmole/g of N-methylmaleimide in squalane, observing reaction rates that were virtually independent of malemide concentration[15], which is consistent with a rate-controlling hydrogen transfer step. While the presence of multiple regioisomers within their products prevented detailed structural analyses, their NMR data suggested that hydrocarbon grafts were comprised of single N-methylsuccinimide units as opposed to short polymer chains.



Scheme 2.2: C-H bond addition of an alkane to NPM

The data listed in Table 2.2 show N-phenylcyclooctylsuccinimide yields depended on the concentration of NPM used in the model compound reaction. As expected, higher monomer concentrations decreased single-graft adduct concentrations from a high of 79% at 14 μmol NPM/g CyOc to a low of 15% at 116 μmol NPM/g CyOc. Although these losses were offset by increases in the yield of multiply-grafted

residue, the monomer content of this fraction did not exceed 1:3.6 of cyclooctane:NPM despite the 10-fold increase in maleimide availabilty. This suggests that NPM oligomerization[16,17] is not a dominant monomer consumption mechanism. Further evidence is provided by the poor agreement of ^{1}H-NMR spectra recorded for multiple-grafted residue (Figure 2.2c) and poly(N-phenylmaleimide) (Figure 2.2d). Our NMR data are more consistent with a mechanism involving intramolecular hydrogen atom abstraction followed by a second NPM addition to give multiple-grafted adducts (Scheme 2.2).

These conclusions are consistent with studies by Knaus et al. on solution-borne reactions of N-phenylethylmalemide and squalane, wherein high monomer concentrations (1:10 ratio of monomer: hydrocarbon) necessitated the use of excess 1,2-dichlorobenzene to maintain a homogeneous condition.[18] Despite the relatively high maleimide loadings used throughout their studies, single graft adducts comprised their principal reaction products, with multiple-graft materials comprising just 25% of converted monomer.

In the context of saturated polymer cross-linking, our model compound studies suggest that the efficiency of C-H bond addition to maleimide will dictate cross-linking yields. Based on the information summarized in Scheme II, the cure boost generate from BMI will depend on two factors – the hydrogen atom donation reactivity of the polymer, and the rate of maleimide addition to the resulting macroradical. The more reactive a given polymer is toward hydrogen atom donation to initiator-derived radicals, the greater the population of macroradical intermediates capable of maleimide grafting. Therefore, our observed reactivity series of PEO > LLDPE > PIB (Table I) can, in part, be rationalized on the basis of initiation efficiency. However, C-H bond addition also involves hydrogen atom transfer to succinimdyl radicals, meaning that good hydrogen atom donors stand to benefit from improved kinetic chain lengths for maleimide addition. Since this hydrogen transfer can contribute to several grafting

turnovers and suppresses maleimide oligomerization, it is expected to be the dominant abstraction process involved in maleimide coagent crosslinking.

The second factor related to polymer structure/reactivity is the rate of macroradical addition to maleimide functionality (Scheme 2.2). The radical additions supported by all three of our saturated polymers are expected to be exothermic. Furthermore, their alkyl macroradicals are relatively nucleophilic, making the addition to an electron-deficient maleimide favourable from the standpoint of polar effects. PEO is an interesting example, since it suffered a severe molecular weight loss when exposed to DCP alone, but a dramatic increase in storage modulus when treated with DCP + BMI (Table I). Rapid macroradical addition to maleimide would force the succinimidyl radical to be the chain carrying intermediate (Scheme 2.2).[19] With an efficient means of quenching a population of fragmenting alkyl macroradicals, chain scission can be suppressed in favour of coagent-induced cross-linking.[20]

2.3.2 Cross-linking of unsaturated polymers

The data plotted in Figure 2.1 show that cis-polybutadiene (PBD) is more responsive than LLDPE to peroxide-only and BMI-assisted cross-linking formulations. Insight into the chemistry that underlies a BMI + PBD cure is provided by the rheological data presented in Figure 2.3a. These experiments included an NPM formulation to investigate the efficacy of a mono-maleimide as a cure-promoting additive. Surprisingly, the NPM formulation was nearly as good as BMI when activated by DCP at 160°C. While it likely that the superiour solubility of NPM plays some role, it is quite remarkable that a mono-functional reagent can fulfill a “coagent” role for this polymer system.

Complementary information is provided in Figure 2.3b. The cyanoalkyl radical generated by AIBN decomposition is resonance stabilized and has a low hydrogen atom abstraction efficiency, preferring

C=C addition to hydrogen transfer.[21] In the absence of coagent, AIBN did not initiate an efficient cure at 100°C, suggesting that cross-linking through the oligomerization of C=C functionality is minimal. However, both NPM and BMI produced substantial gains in cross-link density under identical reaction conditions. Given the limited propensity of this initiator system to activate the polymer by hydrogen atom abstraction, a mechanism other than C-H bond addition to maleimide must be considered.[22]

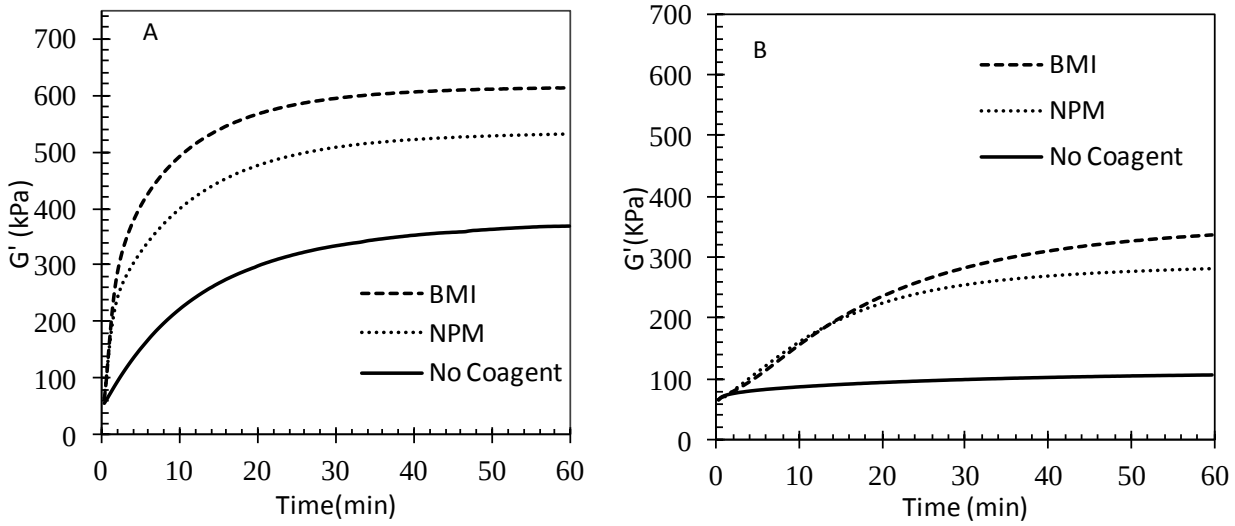


Figure 2.3: Dynamics of coagent assisted crosslinking of PBD at A.160°C (3.6 µmol/g of DCP; 72µmol/g of coagent); B.101°C (3.6 µmol/g of AIBN; 72 µmol/g of coagent)

The key to understanding maleimide cures of unsaturated polymers was gained through model compound experiments. Cis-cyclooctene solutions containing small amounts of NPM were heated with 3.6 µmol/g of DCP at 160°C for 30 min. The reaction products were isolated from residual reagents by precipitation from n-hexane and drying under vacuum. The ^{1}H NMR spectrum of the isolated product (Figure 2.4) shows no evidence of residual olefinic functionality, ruling out C-H bond addition to maleimide as an important reaction pathway. Further information on reaction yields and product compositions is presented in Table 2.3. Note that, irrespective of the amount of monomer charged to the reaction, NPM conversions were quantitative, and product compositions remained in the narrow range of 45% to 51% maleimide, as determined by elemental analysis and confirmed by ^{1}H-NMR spectroscopy.

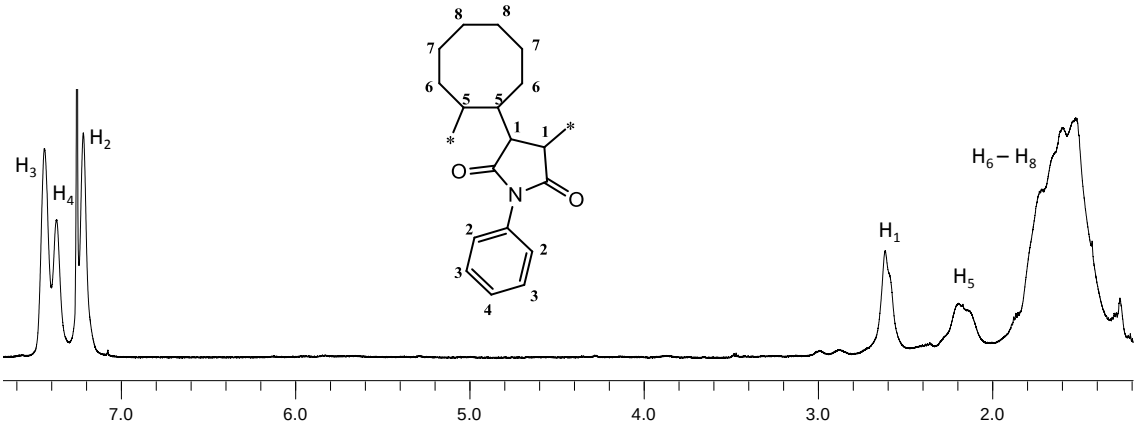


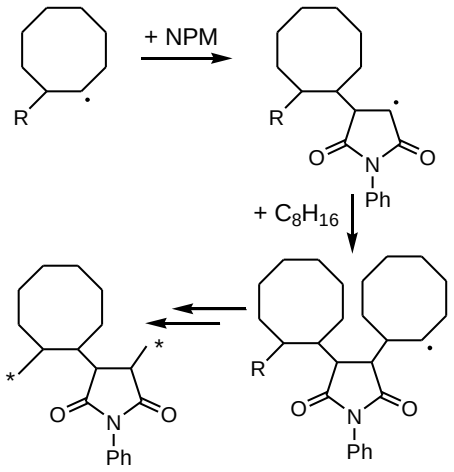
Figure 2.4: ^{1}H NMR spectrum ($CDCl_3$) of poly(cis-cyclooctene-alt-N-phenylmaleimide)

Table 2.3: copolymerization *cis*-cyclooctene and N-phenylmaleimde

NPM loading (µmol/g)	NPM Conversion (%)	Copolymer Elemental Analysis C:H:N:O	Copolymer Composition (% NPM)	Copolymer T_g (°C)
14.5	100	75.56:7.58:4.98:11.01	45	155
29	100	75.96:7.79:4.76:11.96	47	155
58	100	75.36:7.81:4.68:11.09	48	160
116	100	75.95:8.13:4.49:11.08	51	176

[DCP] = 3.6 µmol/g; T=160 °C; t=30 min.

This NMR and elemental analysis data is consistent with poly(cyclooctene-alt-N-phenylmaleimide), an alternating copolymer generated by the radical mechanism shown in Scheme III. Examples of alternating copolymerization are widespread for maleic anhydride,[23] but reports also exist for N-substituted maleimides reacting with isobutene,[24] 2,4,4-trimethylpentene,[25] cyclohexene,[26] and other donor monomers.[27] Our data are remarkable in that an alternating composition is maintained at very low NPM loadings. Unlike the aforementioned copolymerization studies that seek high polymer yields, our reagent concentrations are designed to mimic polymer cure formulations. Fortunately, our model compound results are consistent with the cure rheometry presented in Figure 2.3, in that a small amount of maleimide generate extensive PBD cross-linking.



Scheme 2.3: Alternating copolymerization of cyclooctene and NPM

It is worth noting that the initiator requirements for copolymerizing NPM, and cross-linking PBD, are relatively small, indicating that propagation must be fast relative to radical termination. Similar efficiencies are reported for alternating copolymerizations of maleic anhydride with styrene, which are known to form activated charge-transfer complexes.[28,29] The close association between donor-acceptor monomer combinations leads to strictly alternating copolymerizations of the type observed in this work.[30] Our repeated attempts to identify charge transfer complexes between cyclooctene and NPM using NMR and UV-vis spectroscopy did not provide evidence of their formation, presumably due to the weaker interaction between these monomers. Nonetheless, it is likely that the association of maleimide with abundant C=C functionality promotes the observed copolymerization behaviour observed in this work.

The cross-link yields recorded for different formulations of cis-poly(isoprene) (PIP) and poly(isobutylene-co-isoprene) (IIR) are listed in Table 2.1 alongside those of PBD. The changes in storage modulus ($\Delta G' = G'_{final} - G'_{initial}$) observed for a peroxide-only cure of PIP was 78 kPa, much less than that seen for PBD. This is consistent with other studies[5,6] and suggests that simple C=C oligomerization is not as

efficient in PIP, owing to steric effects imposed by the three substitutents. Interestingly, the inclusion of BMI improved the peroxide cure of PIP comparably to that of PBD. A preliminary model compound study, involving heating a hexane solution containing 0.66 mmole/g of 2-methyl-2-pentene, 0.066 mmole/g of NPM and 0.0033 mmole/g DCP to 160°C for 30 min provided some insight. All NMR evidence of olefinic functionality disappeared, leaving a fully saturated product comprised of converted monomers. This suggests that an alternating copolymerization mechanism may be operative in maleimide-assisted PIP cures, albeit of lower efficiency than seen for PBD.

IIR is a random copolymer of isobutylene and isoprene, whose unsaturation makes the polymer amenable to sulfur vulcanization. The 2.8% of residual C=C functionality within our sample did not support a peroxide-only cure, as macroradical scission was more extensive than cross-linking through radical combination. The presence of BMI had a positive effect, giving $\Delta G' = 16$ kPa, which is below the cross-link density required for consumer goods applications. Some evidence exists that higher isoprene contents render IIR more responsive to peroxide curing,[31] and work is continuing along this line of research.

2.4. Conclusions

N-arylmaleimide coagents engage saturated polymers such as LLDPE through C-H bond addition, the efficiency of which may be affected by the polymer's reactivity toward hydrogen atom donation. In contrast, unsaturated polymers can be cross-linked by an alternating copolymerization that is affected by the unsaturation content of the material as well as the degree of substitution about its C=C functionality.

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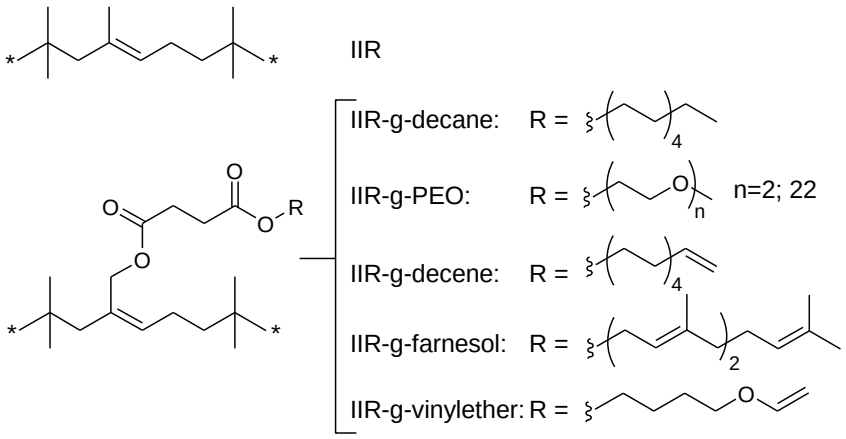
Chapter 3 : Design, Synthesis and Characterization of Bismaleimide Co-curing Elastomers

3.1 Introduction

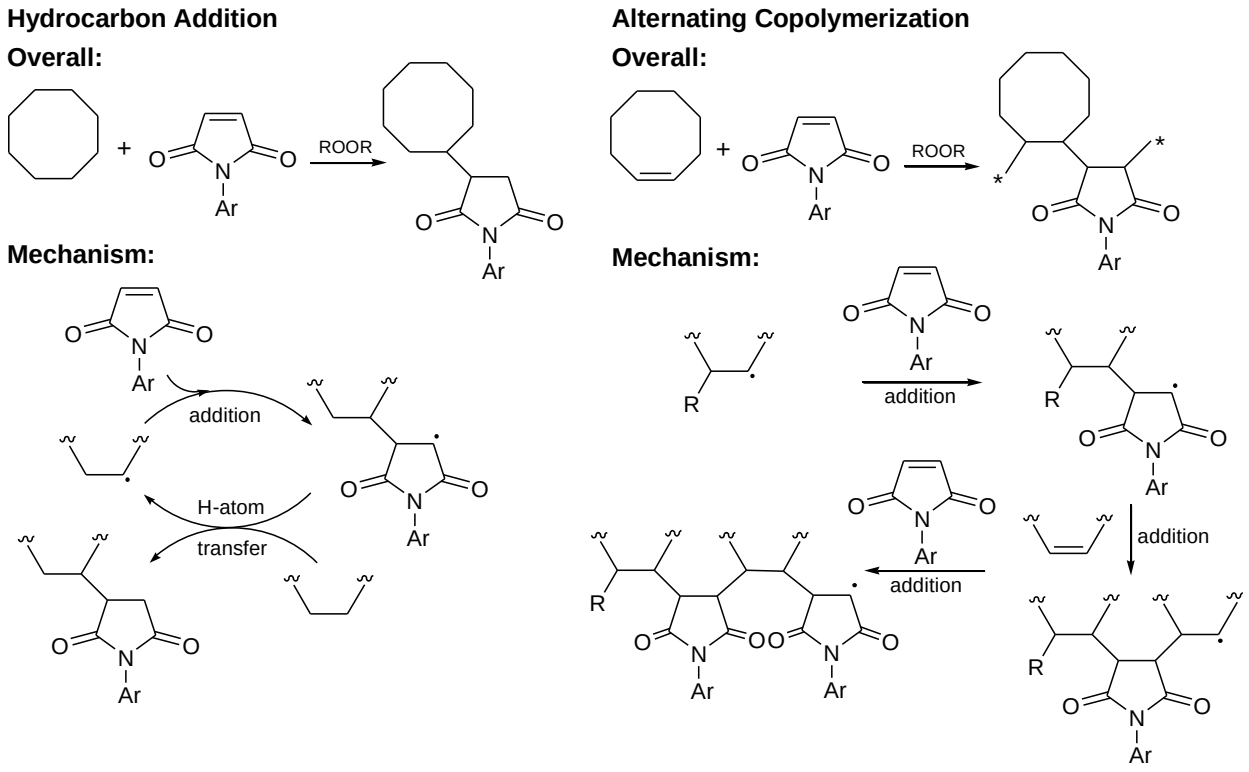
Radical-mediated polymer modifications are robust and inexpensive methods for transforming commodity polymers into value-added materials.[1] A leading example is the peroxide-initiated cross-linking of polyolefins to produce thermoset articles that provide improved modulus, stress relaxation properties, and high-temperature performance.[2] In their simplest form, peroxide cures activate saturated polymers through hydrogen atom abstraction, yielding macroradical intermediates whose combination yields carbon-carbon crosslinks.[3] Peroxide-only formulations of unsaturated materials such as cis-polybutadiene are more complex, however, owing to the potential for C=C bond oligomerization as a means of polymer cross-linking.[4]

This report is concerned with the free radical cross-linking of isobutylene-rich elastomers. Unlike saturated polymers such as poly(ethylene-co-propylene) and hydrogenated nitrile butadiene rubber, polyisobutylene (PIB) is not amenable to peroxide cross-linking, as molecular weight losses suffered as a result of macroradical scission exceed molecular weight gains through macroradical combination. As a result, PIB degrades under the action of peroxide initiators.[5] Copolymerization of isobutylene with small amounts of isoprene (IP) yields an elastomer, butyl rubber (IIR, Scheme 3.1), that can be sulfur-cured, but it does not contain a sufficient amount of residual unsaturation to support peroxide cross-linking. Using dilute solution viscosity as a measure of polymer molecular weights, Loan demonstrated that isoprene contents on the order of 3 mole% mark the transition from a polymer that degrades to one that cross-links to a small extent when treated with dialkyl peroxides.[6]



Scheme 3.1: Reactive functionality in IIR and its designed co-curing derivatives

More recent work has shown that high isoprene grades of IIR (4-8 mole% IP) cure significantly when activated with maleimide-based coagents such as N,N'-m-phenylene dimaleimide (BMI).[7] Since these high-IP materials do not cure efficiently in the absence of coagent, they are classified as "co-curing polymers", whose cross-linking results from reactions of maleimide and isoprene-derived functionality. In a broader sense, an ideal co-curing polymer is unreactive in the absence of a coagent, but is highly reactive when compounded with BMI, curing rapidly and to high extent when initiated by small amounts of peroxide. Furthermore, it is desirable that the peroxide cure consume all maleimide and co-curing polymer functionality, since thermosets that are free of residual reactive groups tend to provide better long-term service performance.



Scheme 3.2: Known C-H bond addition and alternating copolymerization reactions of N-arylmaleimides.[8]

This work provides insight into co-curing reactions of high-IP grades of IIR with BMI, and describes the design of improved co-curing functionality that draws on recently acquired knowledge of N-arylmaleimide chemistry. Previous studies have shown that monomers such as N-phenylmaleimide do not homo-polymerize readily, preferring C-H bond addition to saturated hydrocarbons, and alternating copolymerization with monomers that contain electron-rich C=C functionality (Scheme 2).[8] Therefore, the introduction of appropriate functional groups to an isobutylene-rich polymer backbone should provide elastomers that co-cure with BMI. To this end, we describe the synthesis of a range of IIR derivatives (Scheme 3.1) that engage maleimides in C-H bond addition and/or alternating copolymerization, and assess these new materials in terms of their co-curing reactivity and yields.

3.2. Experimental Section:

Materials: Tetrabutylammonium bromide (98%), 1M tetrabutylammonium hydroxide in methanol, succinic anhydride (97%), dodecanol (98%), farnesol (95%), polyethyleneglycol monomethylether (Mn = 750 g/mole), 9-decen-1-ol (90%), N,N'-(1,3phenylene)dimaleimide (97%), dicumyl peroxide (98%), 1,4-butanediol vinyl ether (99%) were used as received from Sigma-Aldrich. Diethylene glycol monomethyl ether (99%) was used as received from TCI. BIIR (LANXESS Bromobutyl 2030, allylic bromide content ~0.15 mmol/ g), IIR2 (isoprene content ~ 0.35mmol/g), IIR4 (isoprene content ~ 0.71mmol/g) and IIR6 (isoprene content ~ 1.01 mmol/g) were provided by LANXESS Inc. (Sarnia, ON).

Synthesis of IIR-*g*-dodecyl succinate: 1-Dodecanol (1.5 g, 11.8 mmol) and succinic anhydride (1.7 g, 17.7 mmol) were dissolved in toluene (10 g) and heated to 80°C for 4hr. Residual starting materials and solvent were removed by Kugelrohr distillation (T= 80°C, P=0.6 mmHg). The resulting acid-ester was isolated and dried. ^{1}HNMR ($CDCl_3$): δ 2.65 (m, HOOC-C**H$_2$**-CH_2-COO-, 2H), δ 2.59 (m, HOOC-CH_2-C**H$_2$**-COO-, 2H), δ 4.06 (t, -CH-COO-C**H$_2$**-, 2H), δ 1.71 (m, -COO-CH_2-C**H$_2$**-, 2H), δ 1.36 (m, -COO-$(CH_2)_{10}$-C**H$_2$**-CH_3, 2H), δ 1.25 (m, -CH_2-(C**H$_2$**)$_9$- CH_2-CH_3, 18H), δ 0.87 (t, CH_2-C**H$_3$**, 3H); HR-MS calculated for $C_{16}H_{30}O_4$ m/z: 286.2150, found m/z : 286.2144; m.p : 45° - 47°C.

Monododecyl succinic acid (1.37 g, 4.8 mmol) was treated with a 1M solution of Bu_4NOH in methanol (4.8 ml, 4.8 mmol Bu_4NOH) to yield the desired Bu_4Ncarboxylate salt, which was isolated by removing methanol under vacuum. BIIR (16 g) and Bu_4NBr (0.77 g, 2.4 mmol) were dissolved in toluene (150 g) and heated to 85°C for 180 min. Bu_4Ncarboxylate salt (2.5 g, 4.8 mmol) was added before heating the reaction mixture to 85°C for 60 min. The esterification product was isolated by precipitation from excess acetone, purified by dissolution/precipitation using hexanes/acetone, and dried under vacuum,

yielding IIR-g-dodecyl succinate. ^{1}H-NMR ($CDCl_3$): δ 3.92 (t, -CH_2-CH_2-COO-C**H_2**-, 2H), δ 3.35 (s, OOC -C**H_2**-C**H_2**-COO-, 4H), δ 4.48 (E-ester, =C-**CH_2**-OCO-, 2H, s), δ 4.50 (Z-ester, =C-**CH_2**-OCO-, 2H, s)

Synthesis of IIR-g-farnesyl succinate: Farnesol (2 g, 9.0 mmol) and succinic anhydride (1.0 g, 9.9 mmol) were dissolved in toluene (10 g) and heated to 80°C for 4hr. Residual starting materials and solvent were removed by Kugelrohr distillation (T= 80°C, P=0.6 mmHg). The resulting acid-ester was isolated and dried. δ 2.65 (m, HOOC-C**H_2-**CH_2-COO-, 2H), δ 2.59 (m, HOOC-CH_2-C**H_2**-COO-, 2H), δ 4.60 (d, -CH_2-COO-C**H_2**-, 2H), δ 5.30(E), 5.06(Z) (t, -C(CH_3)=C**H**-, 3H), δ 2.08-1.94 (m, =CH-C**H_2**-C**H_2**-C(CH_3), 8H), δ 1.67-1.56 (s, -C(C**H_3**)=CH-, 12H); HR-MS calculated for $C_{19}H_{30}O_4$ m/z: 322.2138, found m/z : 322.2144.

Monofarnesyl succinic acid (1.54 g, 4.8 mmol) was treated with a 1M solution of Bu_4NOH in methanol (4.8 ml, 4.8 mmol Bu_4NOH) to yield the desired Bu_4Ncarboxylate salt, which was isolated by removing methanol under vacuum. BIIR (16 g) and Bu_4NBr (0.77 g, 2.4 mmol) were dissolved in toluene (150 g) and heated to 85°C for 180 min. Bu_4Ncarboxylate salt (2.72 g, 4.8 mmol) was added before heating the reaction mixture to 85°C for 60 min. The esterification product was isolated by precipitation from excess acetone, purified by dissolution/precipitation using hexanes/acetone, and dried under vacuum, yielding IIR-g-farnesyl succinate. ^{1}H-NMR ($CDCl_3$): δ 3.92 (t, -CH_2-CH_2-COO-C**H_2**-, 2H), δ 3.35 (s, OOC-C**H_2**-C**H_2**-COO-, 4H), δ 4.48 (E-ester, =C-**CH_2**-OCO-, 2H, s), δ 4.50 (Z-ester, =C-**CH_2**-OCO-, 2H, s).

Synthesis of IIR-g-PEG succinate: polyethyleneglycol monomethylether (14.1 g, 19.4 mmol) and succinic anhydride (2.9 g, 29.5 mmol) were dissolved in toluene (10 g) and heated to 80°C for 4hr. Residual starting materials and solvent were removed by Kugelrohr distillation (T= 80°C, P=0.6 mmHg). The resulting acid-ester was isolated and dried. δ 2.65 (m, HOOC-C**H_2-**CH_2-COO-, 2H), δ 2.59 (m, HOOC-CH_2-C**H_2**-COO-, 2H), δ 4.11 (t, -CH_2-COO-C**H_2**-, 2H), δ 3.60 (t, -C**H_2**-O-C**H_2**-, nH), δ 3.31 (s, -CH_2-O-C**H_3**, 3H).

PEG succinate half-ester (4.07 g, 4.8 mmol) was treated with a 1M solution of Bu_4NOH in methanol (4.8 ml, 4.8 mmol Bu_4NOH) to yield the desired Bu_4Ncarboxylate salt, which was isolated by removing methanol under vacuum.

BIIR (16g) and Bu_4NBr (0.77 g, 2.4mmol) were dissolved in toluene (150 g) and heated to 85°C for 180 min. Bu_4Ncarboxylate salt (5.23 g, 4.8 mmol) was added before heating the reaction mixture to 85°C for 60 min. The esterification product was isolated by precipitation from excess acetone, purified by dissolution/precipitation using hexanes/acetone, and dried under vacuum, yielding IIR-g-PEG succinate. ^{1}H-NMR ($CDCl_3$): δ 3.72 (t, -C**H$_2$**-O-C**H$_2$**-), δ 4.11 (t, -CH_2-CH_2-COO-C**H$_2$**-, 2H), δ 3.35 (s,OOC -C**H$_2$**-C**H$_2$**-COO-, 4H), δ 3.60 (t, -C**H$_2$**-O-C**H$_2$**-, nH), δ 3.31 (s, -CH_2-O-C**H$_3$**, 3H), δ 4.48 (E-ester, =C-**CH$_2$**-OCO-, 2H, s), δ 4.50 (Z-ester, =C-**CH$_2$**-OCO-, 2H, s).

Synthesis of IIR-g- methoxy ethoxy ethyl succinate : Methoxyethoxyethanol (1.5 g, 12.5 mmol) and succinic anhydride (1.87 g, 18.7 mmol) were dissolved in toluene (10 g) and heated to 80° C. for 4 hr. Residual starting materials and solvent were removed by Kugelrohr distillation (T=80° C., P=0.6 mmHg). The resulting acid-ester (1.056 g, 4.8 mmol) was treated with a 1 M solution of Bu_4NOH in methanol (4.8 mL, 4.8 mmol Bu_4NOH) to yield the desired Bu_4Ncarboxylate salt, which was isolated by removing methanol under vacuum δ 2.65 (m, HOOC-C**H$_2$**-CH_2-COO-, 2H), δ 2.59 (m, HOOC-CH_2-C**H$_2$**-COO-, 2H), δ 4.11 (t, -CH_2-COO-C**H$_2$**-, 2H), δ 3.60 (t, -C**H$_2$**-O-C**H$_2$**-, 6H), δ 3.31 (s, -CH_2-O-C**H$_3$**, 3H). HR-MS calculated for $C_9H_{15}O_6$ m/z: 219.0866, found m/z: 219.0868.

BIIR (16 g) and Bu_4NBr (0.77 g, 2.4 mmol) were dissolved in toluene (150 g) and heated to 85° C. for 180 min. The desired Bu4Ncarboxylate salt (2.21 g, 4.8 mmol) was added before heating the reaction mixture to 85° C. for 60 min. The esterification product was isolated by precipitation from excess

acetone, purified by dissolution/precipitation using hexanes/acetone, and dried under vacuum, yielding IIR-g-ether. ^{1}H-NMR ($CDCl_3$): δ 3.72 (t, -C**H$_2$**-O-C**H$_2$**-), δ 4.11 (t, -CH_2-CH_2-COO-C**H$_2$**-, 2H), δ 3.35 (s,OOC -C**H$_2$**-C**H$_2$**-COO-, 4H), δ 3.60 (t, -C**H$_2$**-O-C**H$_2$**-, 6H), δ 3.31 (s, -CH_2-O-C**H$_3$**, 3H),δ 4.48 (E-ester, =C-**CH$_2$**-OCO-, 2H, s), δ 4.50 (Z-ester, =C-**CH$_2$**-OCO-, 2H, s).

Synthesis of IIR-*g*-decenyl succinate: 9-Decen-1-ol (1.5 g, 9.6 mmol) and succinic anhydride (1.2 g, 12.0 mmol) were dissolved in toluene (10 g) and heated to 80°C for 4hr. Residual starting materials and solvent were removed by Kugelrohr distillation (T= 80°C, P=0.6mmHg). The resulting acid-ester was isolated and dried. ^{1}H-NMR ($CDCl_3$): δ 2.65 (m, HOOC-C**H$_2$-**CH_2-COO-, 2H), δ 2.59 (m, HOOC-CH_2-C**H$_2$**-COO-, 2H), δ 4.08 (t, -CH_2-COO-C**H$_2$**-, 2H), δ 5.74 (m, CH_2=C**H**-, 1H), δ 4.93 (dd, C**H$_2$**=CH-, 1H), δ 4.87 (dd, C**H$_2$**=CH-, 1H), δ 1.97 (m, CH_2=CH-C**H$_2$**-CH_2-, 2H), δ 1.64 (m, COO-CH_2-C**H$_2$**-CH_2- , 2H), δ 1.27 (m, =CH-CH_2-$(CH_2)_5$-CH_2-OOC-, 10H); HR-MS calculated for $C_{14}H_{23}O_4$ m/z: 255.1592, found m/z: 255.1596.

Monodecenyl succinic acid (1.22 g, 4.8 mmol) was treated with a 1M solution of Bu_4NOH in methanol (4.8 ml, 4.8 mmol Bu_4NOH) to yield the desired Bu_4Ncarboxylate salt, which was isolated by removing methanol under vacuum. BIIR (16 g) and Bu_4NBr (0.77 g, 2.4 mmol) were dissolved in toluene (150 g) and heated to 85°C for 180 min. Bu_4Ncarboxylate salt (2.37 g, 4.8 mmol) was added before heating the reaction mixture to 85°C for 60 min. The esterification product was isolated by precipitation from excess acetone, purified by dissolution/precipitation using hexanes/acetone, and dried under vacuum, yielding IIR-g-decenyl succinate. ^{1}H-NMR ($CDCl_3$): δ 5.74 (m,-CH_2=C**H**-CH_2-, 1H), δ 4.91 (d, C**H$_2$**=CH-, 1H), δ 4.84 (d ,C**H$_2$**=CH-, 1H), δ 3.92 (t, -CH_2-CH_2-COO-C**H$_2$**-, 2H), δ 3.35 (s,OOC -C**H$_2$**-C**H$_2$**-COO-, 4H), δ 4.49 (E-ester, =C-**CH$_2$**-OCO-, 2H, s), δ 4.50 (Z-ester, =C-**CH$_2$**-OCO-, 2H, s)

Synthesis of IIR-*g*-butanediol vinyl ether succinate: 1,4-butanediol monovinyl ether (4 g, 34.5 mmol) and succinic anhydride (3.6 g, 36 mmol) were dissolved in toluene (10 g)along with triethylamine (3.6g. 35.6 mmol) and heated to 80°C for 4hr. Residual starting materials and solvent were removed by Kugelrohr distillation (T= 80°C, P=0.6mmHg). The resulting triethylammonium carboxylate salt was isolated and dried. ^{1}H-NMR ($CDCl_3$): δ 2.65 (m, HOOC-C**H$_2$**-CH_2-COO-, 2H), δ 2.59 (m, HOOC-CH_2-C**H$_2$**-COO-, 2H), δ 4.08 (t, -CH_2-COO-C**H$_2$**-, 2H), δ 6.45 (dd, CH_2=C**H**-O-, 1H), δ 4.18 (dd, C**H$_2$**=CH-O-, 1H), δ 3.97 (dd, C**H$_2$**=CH-O-, 1H), δ 1.70 (m, -O-CH_2-C**H$_2$**-C**H$_2$**- CH_2-O-, 4H), δ 2.69 (q, (CH_3-C**H$_2$**-)$_3N^+$-H , 2H), δ1.09 (t, (C**H$_3$**-CH_2-)$_3N^+$-H, 3H). HR-MS calculated for $C_{10}H_{15}O_5$ calculated m/z: 215.0915, found m/z: 215.0919.

BIIR (76 g) and Bu_4NBr (3.67g, 11.4 mmol) were dissolved in toluene (750 g) and heated to 85°C for 180 min. Triethyl ammonium carboxylate salt (5.42 g, 17.1 mmol) was added before heating the reaction mixture to 85°C for 60 min. The esterification product was isolated by precipitation from excess acetone, purified by dissolution/precipitation using hexanes/acetone, and dried under vacuum, yielding IIR-g-decenyl succinate. ^{1}H-NMR ($CDCl_3$): δ 6.43 dd,CH_2=C**H**-O-, 1H), δ 4.18 (dd, C**H$_2$**=CH-, 1H), δ 3.92 (dd, C**H$_2$**=CH-, 1H), δ 3.92 (t, -CH_2-CH_2-COO-C**H$_2$**-, 2H), δ 3.35 (s, -OOC -C**H$_2$**-C**H$_2$**-COO-, 4H), δ 4.49 (E-ester, =C-**CH$_2$**-OCO-, 2H, s), δ 4.50 (Z-ester, =C-**CH$_2$**-OCO-, 2H, s).

Synthesis of IIR-g-undecenoate : 10-Undecenoic acid (0.88 g,3.7 mmol) was treated with a 1M solution of Bu_4NOH in methanol (4.8 ml, 4.8 mmol Bu_4NOH) to yield the desired Bu_4Ncarboxylate salt, which was isolated by removing methanol under vacuum. BIIR (16 g) and Bu_4NBr (0.77 g, 2.4 mmol) were dissolved in toluene (150 g) and heated to 85°C for 180 min. Bu_4Ncarboxylate salt (2.04 g, 4.8 mmol) was added before heating the reaction mixture to 85°C for 60 min. The esterification product was isolated by precipitation from excess acetone, purified by dissolution/precipitation using hexanes/acetone, and dried under vacuum, yielding IIR-g-undecenoate. ^{1}H-NMR ($CDCl_3$): δ 5.68 (m,-CH_2=C**H**-CH_2-, 1H), δ 4.85

(d, C**H$_2$**=CH-, 1H), δ 4.79 (d, C**H$_2$**=CH-, 1H), δ 4.51 (E-ester, =CH-**CH$_2$**-OCO-, 2H, s), δ 4.56 (Z-ester, =CH-**CH$_2$**-OCO-, 2H, s)

Instrumentation and Analysis.

^{1}H-NMR spectra were acquired in $CDCl_3$ on a Bruker Avance-600 spectrometer. Mass spectra were obtained from methanol solutions on an Applied Biosystems QStar XL QqTOF mass spectrometer. Dynamic shear modulus, stress relaxation and temperature sweep measurements were recorded using an Alpha Technologies, Advanced Polymer Analyzer 2000. Pressed samples of elastomer were coated with the required amount of a stock solution of DCP in acetone, and allowed to dry prior to passing three times through a 2-roll mill. This mixed compound was cured in the rheometer cavity at 160° C at a 3° oscillation arc and a frequency of 1 Hz to record dynamic shear modulus. The samples for stress realaxation measurements were cured as described by the above procedure followed by subjecting them to a strain of 2°arc at 100°C. Temperature sweeps were recorded on cured samples at a 3° arc and a frequency of 1 Hz.

Tensile measurements were recorded using an INSTRON Series 3360 Universal Testing Machine operating at a crosshead speed of 500 mm/min. A 40g rubber sample was mixed with required amount of DCP and coagent using a Haake Polylab R600 internal batch mixer at 50°C for 10 min. The samples for tensile measurements were cut from a cured sheet of 2mm thickness, prepared by compression molding 35g of rubber sample at 160°C for 30 min at a pressure of 20 MPa.

3.3. Results and Discussion

3.3.1 High Isoprene IIR

Time-resolved measurements of the dynamic storage modulus (G') at fixed temperature, frequency, and shear strain amplitude, provide a standard means of assessing the dynamics and yield of polymer cross-linking processes.[9] Figure 3.1 illustrates such data for dicumylperoxide (DCP) cures as well as DCP + BMI formulations for a range of IIR grades as well as two benchmark polymers, polyisobutylene (PIB) and cis-polyisoprene (PIP), which sit at opposite ends of the isoprene content spectrum. Treating these benchmarks with 3.6 μmole DCP / gram elastomer at 160°C produced the expected responses, with PIB undergoing significant degradation, and PIP curing substantially (Figure 3.1a). The inclusion of 0.075 mmole BMI/g in these cure formulations only reduced the degradation rate of PIB, while the cure rate and extent observed for PIP was improved substantially by bis-maleimide coagent (Figure 3.1b).

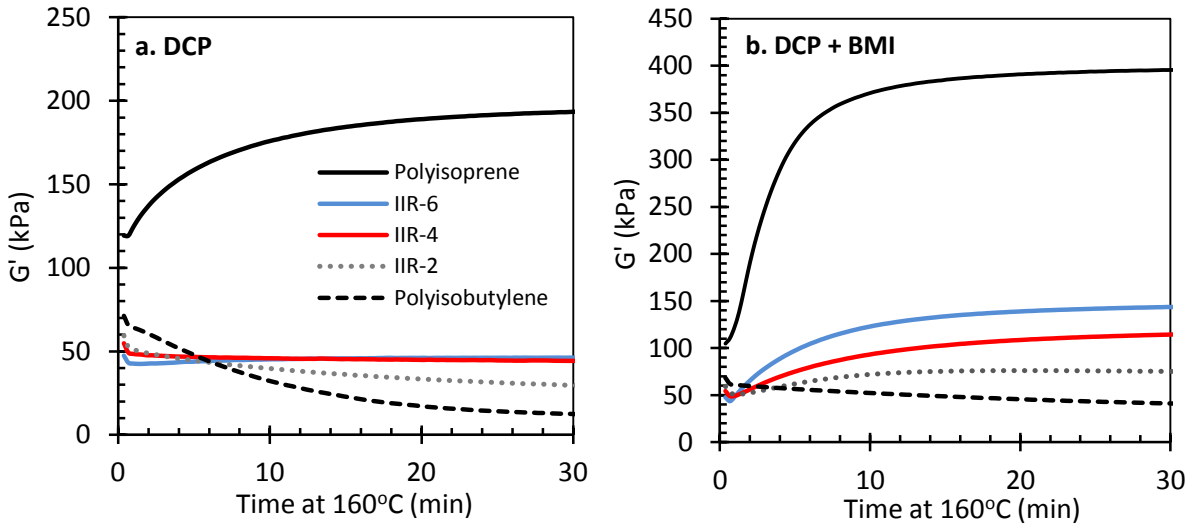


Figure 3.1 Dynamics of peroxide-initiated cross-linking of PIB, PIP, and IIR grades of different IP content (a. [DCP]=3.70 μmole/g; b. [DCP]=3.70 μmole/g, [BMI] = 0.075 mmole/g).

The inability of PIB to cure in the presence of BMI is likely due to its inefficiency in C-H bond addition to maleimides. As noted above, saturated polymers are activated in peroxide cures through hydrogen atom abstraction by peroxide-derived radical intermediates. Coagent grafting proceeds through a

closed sequence of two reactions; macroradical addition to maleimide, and hydrogen atom abstraction by the resulting succinimidyl radical (Scheme 3.2).[1,10] Reports of PIB addition to maleic anhydride, a reaction that is closely related to maleimide grafting, have demonstrated the poor reactivity of PIB in such processes.[11,12] This inefficiency may stem from the low reactivity of PIB toward hydrogen atom donation, a characteristic that makes this polymer particularly stable toward oxidative degradation.[13] Since hydrogen transfer from PIB to succinimidyl radical intermediates is required to close the propagation sequence of maleimide addition, slow hydrogen atom donation would make BMI grafting uncompetitive with macroradical scission, thereby resulting in the G' loss shown in Figure 3.1b.

The peroxide vulcanization of PIP has received considerable attention, and is reported to progress through allylic hydrogen atom abstraction by initiator-derived radicals, followed by macroradical combination.[14,15] Cross-linking by oligomerization of its isoprene-derived C=C unsaturation is believed to be minimal for this polymer, unlike cis-polybutadiene that cures more efficiently at a given initiator loading.[16] Regardless, the data presented in Figure 3.1 demonstrate the superiour cross-linking activity of PIP over PIB when cured by DCP alone, and when DCP is used in combination with BMI.

In our previous study of maleimide cure chemistry, the importance of alternating copolymerization between C=C unsaturation in the polymer backbone and the coagent (Scheme 3.2) was demonstrated by cure rheology studies involving N-phenylmaleimide (NPM), a mono-functional molecule.[8] We showed that NPM is nearly as effective as BMI in cis-polybutadiene cures, producing comparable cross-link densities when compounded into the elastomer at the same maleimide concentration. Table 3.1 summarizes cross-linking extent data for a range of polymers and cure formulations. Of present interest is the cross-link yield ($\Delta G' = G'_{max} - G'_{initial}$) for PIP cure formulations employing DCP, DCP+NPM and

DCP+BMI. These data show that NPM provided $\Delta G'$=82 kPa, substantially lower than observed for BMI (260 kPa), but significantly greater than seen for DCP alone (69 kPa).

Table 3.1 Summary of cross-linking extents

Polymer	Isoprene Content (mmole/g)	Functional Group Content (mmole/g)	$\Delta G'$ DCP only (kPa)[a]	$\Delta G'$ DCP+NPM (kPa)[b]	$\Delta G'$ DCP+BMI (kPa)[c]	BMI Increment (kPa)[d]
PIB	0.00	---	-54	-26	-25	29
IIR-2	0.35	---	-26	-31	25	51
IIR-4	0.71	---	-5	4	69	74
IIR-6	1.01	---	5	13	94	89
PIP	14.7	---	69	82	260	191
IIR-dodecane	0.11	0.15	-23	-18	90	113
IIR-PEG_{120}	0.11	0.30	-8	-5	132	140
IIR-PEG_{750}	0.11	2.60	4	3	210	206
IIR-farnesol	0.11	0.45	5	8	92	87
IIR-decene	0.11	0.15	5	12	105	100
IIR-vinylether	0.11	0.15	34	183	281	247

a. [DCP]=3.70 μmole/g, 160°C
b. [DCP] = 3.70 μmole, [NPM] = 0.075 mmole/g, 160°C
b. [DCP] = 3.70 μmole, [BMI] = 0.075 mmole/g, 160°C
d. BMI Increment = $\Delta G'_{DCP+BMI}$-$\Delta G'_{DCP}$

Further insight into reactions of PIP and N-arylmaleimides was gained from the characterization of products derived from 2-methyl-2-pentene, a model compound for the unsaturation within the polymer. A benzene solution containing 0.66 mmole/g of 2-methyl-2-pentene, 0.066 mmole/g of NPM and 3.3 μmole/g DCP was heated to 160°C for 30 min in a pressurized autoclave before removing residual solvent and unconverted olefin. ^{1}H-NMR analysis showed unconverted NPM and a mixture of maleimide-derived products that contained relatively little C=C unsaturation (See Supporting Information). This suggests that 2-methyl-2-pentene and NPM react predominately by copolymerization. Steric inhibition of radical addition reactions are well documented,[17,18] and may underlie the lower reactivity of the tri-substituted olefin within PIP compared to the di-substituted

functionality found in cis-polybutadiene. This issue is revisited in the following section dealing with co-curing polymer design.

Given these observations of PIB and PIP cross-linking, it is not surprising that introducing isoprene to an isobutylene-rich elastomer improves peroxide cure performance. However, the rheology data presented in Figure 3.1a show that higher IP contents do not support peroxide-only formulations. Rather, the isoprene unsaturation present within IIR only mitigates peroxide-induced degradation, and coagent is needed to produce significant cross-linking extents. The BMI formulation data illustrated in Figure 1b are consistent with reports of Resendes and coworkers,[19] in that high-IP grades of IIR were cured by a combination of DCP+BMI. Cure yields were far below those provided by PIP, but were consistent with expectations based on the low isoprene content of these materials (Table 3.1).

The effect of isoprene content on the cure performance of IIR is illustrated in Figure 3.2, which presents plots of the change in storage modulus ($\Delta G' = G'_{max} - G'_{initial}$) recorded for DCP-only and DCP+BMI formulations. Figure 3.2a summarizes data acquired with [DCP] = 3.7 μmole/g, while Figure 3.2b presents data measured at an initiator loading 5 times greater at [DCP] = 18.5 μmole/g. Consistent with the findings of Loan,[6] isoprene contents in the range of 6 mole% (1.06 mmole/g) were needed before IIR will not degrade when treated with DCP at 160°C. Of greater interest are the yields provided by BMI, both in absolute terms and relative to the peroxide-only formulation.

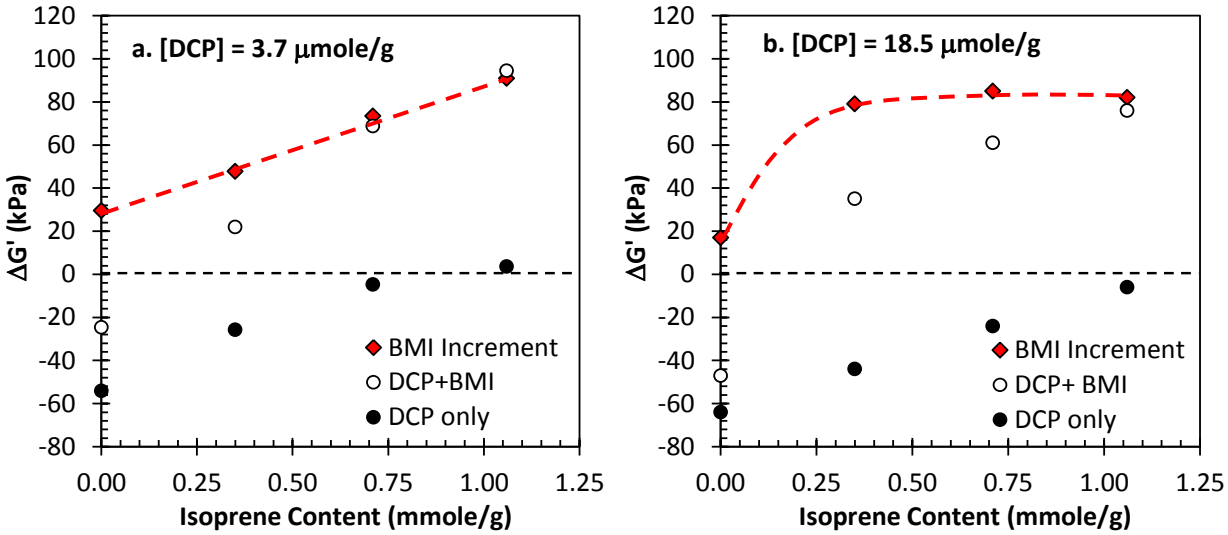


Figure 3.2 Cure yields for DCP-only and DCP+0.075 mmole BMI/g formulations as a function of IIR isoprene content (160°C, 1 Hz, 3° arc)

Since coagent is needed to produce a cross-linked polymer network within IIR, cure extent is maximized when BMI conversions are quantitative, and when they are directed toward the coupling of IIR chains. This requires an initiator loading that is sufficient to support complete maleimide conversion, and a co-curing polymer that is sufficiently reactive toward maleimide to engage BMI in cross-linking. The data plotted in Figure 3.2a show that at a low DCP loading of 3.7 µmole/g, coagent utilization is sensitive to the isoprene content of the elastomer. Absolute values of cure extent (ΔG'), and the increment provided by BMI ($\Delta G'_{DCP+BMI}-\Delta G'_{DCP}$), increased linearly with IIR unsaturation. Therefore, when only a small amount of initiator is supplied, BMI requires excess isoprene to support the copolymerization process.

Different behaviour is observed at a higher DCP loading of 18.5µmole/g. The data plotted in Figure 3.2b show that absolute ΔG' values scaled linearly with IP content, but BMI increments did not vary amongst our three IIR samples. In each case ($\Delta G'_{DCP+BMI}-\Delta G'_{DCP}$) values remained constant at about 82 kPa. This shows that if a BMI cure formulation is given sufficient initiator, full coagent utilization can be reached

with relatively low IP contents. Any further increases in isoprene levels serve only to promote the conventional IIR coupling process, since they are not needed to promote maleimide conversion.

We note that the design of peroxide-curable grades of IIR has parallels with the 1950's introduction of fast sulfur curing grades for the tire inner liner market. While IIR containing 2% IP can be vulcanized by standard sulfur formulations, it does not cure as rapidly as the diene-rich elastomers that comprise other tubeless tire components. This problem was solved not by increasing isoprene contents, but by halogenating IIR to introduce an allylic halide electrophile that reacts readily with sulfur nucleophiles.[20,21] By analogy, coagent curable grades of IIR need not contain excessive amounts of isoprene if they contain functionality that engages N-aryl maleimides in efficient free radical, co-curing chemistry.

3.3.2 Co-curing Elastomer Design

Designing a co-curing elastomer requires the identification of functionality that reacts with BMI, and the development of a method to introduce this functionality to an isobutylene-rich polymer backbone. The synthesis of such isobutylene-rich elastomers is complicated by the intolerance of cationic isobutylene polymerizations to polar and/or mildly acidic reagents.[22] Therefore, we chose a post-polymerization, chemical modification approach involving nucleophilic halide displacement from brominated poly(isobutylene-co-isoprene), or BIIR. Many of the functional groups of interest are available as primary alcohols and, while direct etherification of BIIR is possible,[23,24] esterification can be conducted under milder conditions, thereby providing better yields.[25] Therefore, we prepared half-esters of hydroxyl-terminated reagents by ring-opening of succinic anhydride. These were then used to produce the succinate diesters shown in Scheme 3.1. The BIIR used throughout this work contained 0.15 mmoles of allylic bromide functionality and 0.11 mmoles of residual isoprene unsaturation per gram of polymer,

both distributed randomly amongst polymer chains. Since our esterifications were conducted to full conversion, our functionalized IIR materials contained 0.15 mmoles of succinate diester and 0.11 mmoles isoprene unsaturation per gram of polymer.

The contribution of succinate diester and residual isoprene unsaturation within our co-curing polymers was gauged with a reference material, IIR-g-dodecane that cannot engage in alternating copolymerization, and should not be particularly reactive in C-H bond additions. Interestingly, this control material degraded when treated with peroxide alone (Figure 3a), but cured to $\Delta G' = 90$ kPa when compounded with DCP+BMI (Figure 3.3b). This cross-link density approached the value provided by IIR6 ($\Delta G' = 94$ kPa, Table 3.1), which serves only as further evidence of high-IP butyl inactivity. Much more effective co-curing functionalities are described in the sections that follow.

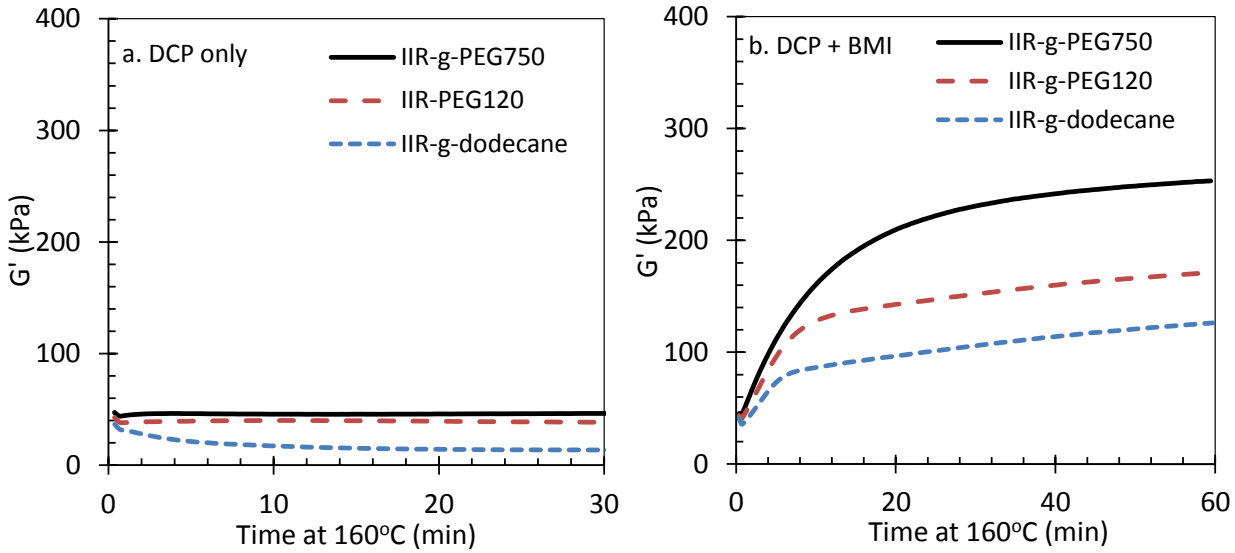


Figure 3.3: Dynamics of peroxide-initiated cross-linking of saturated IIR-g-succinate elastomers (a. [DCP]=3.70 μmole/g; b. [DCP]=3.70 μmole/g, [BMI] = 0.075 mmole/g).

3.3.2.1 C-H Bond Addition Strategies

This approach to co-curing polymer design requires functionality that supports efficient hydrogen atom transfer and radical addition reactions (Scheme 3.2). Inactivity in either component of this propagation sequence will result in poor kinetic chain length for maleimide grafting,[26] and small coagent-assisted cure yields. Polyethers provide the low C-H bond dissociation energy (BDE) needed for rapid hydrogen atom abstraction. Consider the reported BDE value for H-2-tetrahydrofuranyl (385 kJ/mol), compared to that of H-cyclohexyl (400 kJ/mol).[27] Furthermore, alkyl radicals derived from hydrogen atom abstraction from polyethers are relatively nucleophilic,[28] thereby promoting their addition to electron-deficient monomers.[29] Our previous studies of BMI cure chemistry showed that polyethylene oxide degrades considerably when treated with peroxide alone, but cross-links extensively in the presence of BMI.[8] Therefore, grafting polyether functionality to an isobutylene-rich backbone may be expected to yield an elastomer that is not cross-linked efficiently by peroxide alone, but co-cures extensively when combined with BMI.

We prepared two samples to IIR-PEG to illustrate the potential utility of polyether graft copolymer derivatives of BIIR. One sample contained 2 ethylene glycol mers per side chain (IIR-g-PEG120) and the other with 22 ethylene oxide mers per side chain (IIR-g-PEG750). The response of these materials to radical cure formulations is illustrated in Figure 3.3. As expected, neither graft copolymer cured in the peroxide-only formulation, since both the IIR backbone and PEG side chains are susceptible to radical degradation. Inactivity in a peroxide-only formulation is a desirable outcome of a co-curing polymer design. A material that does not respond to peroxide alone is less likely to engage in oxidative cross-linking when stored for prolonged periods in the uncured state, and during its active service life in a thermoset condition. From this perspective, the inactivity of IIR-PEG to DCP bodes well for the storage and service stability of this class of co-curing elastomer.

Of equal or greater importance is the activity of the material when compounded with BMI. The data presented in Figure 3.3b show that both polyether functionalized elastomers cured significantly when mixed with coagent, with IIR-PEG_{750} generating $\Delta G'$ = 210 kPa. Moreover, the BMI increment for this polymer was ($\Delta G'_{DCP+BMI}$-$\Delta G'_{DCP}$) = 206 kPa – amongst the highest recorded in this study. This is clear evidence of the heightened efficiency that can be realized when using appropriate co-curing functionality. Since this co-curing strategy requires a di-functional coagent to produce cross-links, NPM provided no enhancement to the observed modulus change (Table 3.1).

3.3.2.2 Copolymerization Strategies

Alternating copolymerizations of N-substituted maleimides reacting with isobutene,[30] 2,4,4-trimethylpentene,[31] cyclohexene,[32] and other donor monomers[33] are well documented, and our analysis of 2-methyl-2-pentene + NPM reaction products suggests that copolymerization is a contributor to the reactivity of high-IP grades of IIR. However, inefficiencies in the IIR system are evident from the relatively poor performance of NPM as a curative, thereby fueling our interest in C=C functionality that engages maleimides in more efficient radical copolymerizations.

IIR-g-farnesol was prepared as a succinate diester derivative of BIIR (Scheme 3.1). It contained 0.11 mmole/g of single isoprene mers within the polymer backbone, and 0.45 mmole/g of pendant isoprene trimers, both distributed randomly. Figure 3.4a shows that the storage modulus of this material was unaffected by DCP, as the elastomer suffered no net degradation or cross-linking at 160°C. Compounding IIR-g-farnesol with BMI produced a coagent-assisted cure of $\Delta G'$ = 92 kPa (Figure 3.4b), which is nearly identical to that provided by IIR-6, which provided nearly twice the unsaturation content (Table 3.1). This shows that pendant functionality is more effective than backbone unsaturation, either

due to enhanced mobility and/or the lack of steric crowding imposed by adjacent isobutylene mers in the polymer chain.

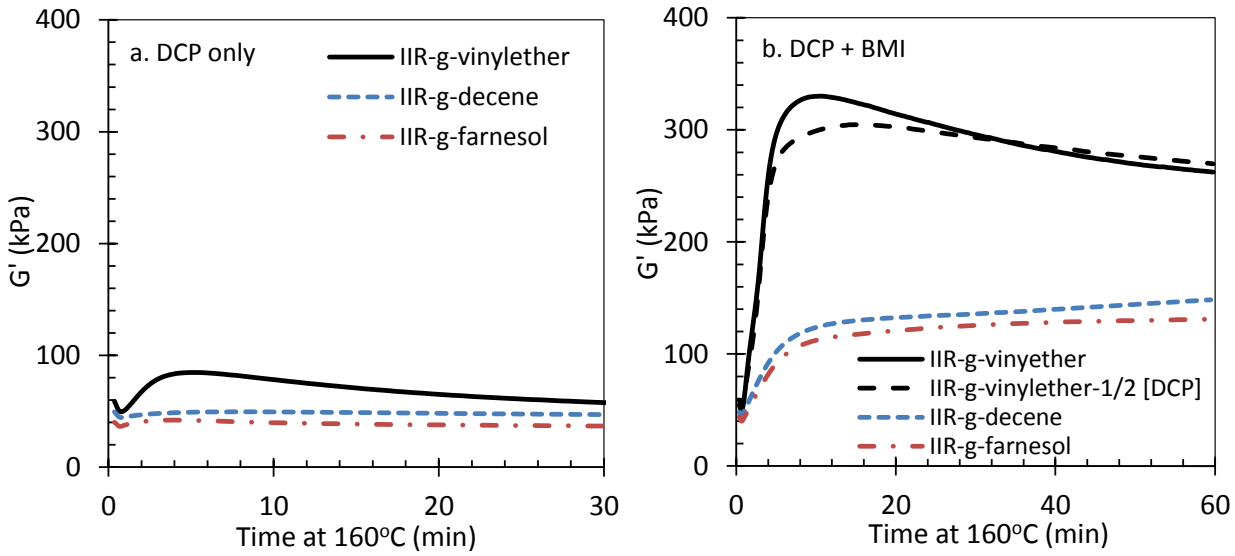


Figure 3.4 Dynamics of peroxide-initiated cross-linking of unsaturated IIR-g-succinate elastomers (a. [DCP]=3.70 μmole/g; b. [DCP]=3.70 μmole/g, [BMI] = 0.075 mmole/g).

The cure performance provided by the terminal olefin functionality within IIR-g-decene is instructive. Unactivated α-olefins do not homopolymerize readily, owing to degradative chain transfer by allylic hydrogen atom abstraction.[34] However, alternating copolymerizations benefit from polar interactions of electron-rich olefins and electron-deficient N-substituted maleimides.[35] The co-agent cure data illustrated in Figure 3.4 confirm that IIR-g-decene is not reactive alone, but cures readily in a BMI formulation. As such, this material demonstrates the desirable attributes of a co-curing polymer – good storage stability, and high coagent cure reactivity. A commercially more attractive preparation of such a material involves the esterification of 10-undecenoic acid, a nylon-11 precursor, with BIIR to introduce terminal vinyl functionality. The BMI-assisted cure of this material, IIR-undecenoate, was indistinguishable from that of IIR-decene, providing a $\Delta G'$ = 90 kPa.

Vinyl ethers are the most electron rich olefins examined in this work. A leading study concerning the copolymerization of vinyl ethers and maleimides was reported by Olson and Butler, who prepared highly alternating copolymers from NPM and 2-chloroethyl vinyl ether using conventional free radical initiation.[36] The charge transfer band discovered by UV analysis of monomer mixtures revealed a relatively strong donor-acceptor interaction that is believed to underlie the reactivity of this system as well as its alternating nature. In the present context, the functionality within IIR-vinyl ether was expected to engage both NPM and BMI alternating copolymerization, leading to extensive cross-linking.

The cure rheology data provided in Figure 3.4 are consistent with these expectations. When initiated by DCP alone, IIR-g-vinyl ether demonstrated some cross-linking activity, followed by a period of mild cure reversion. This is commonly observed for macromonomer derivatives of IIR that bear polymerizable acrylic or styrenic functionality.[37] In these systems, peroxide amounts beyond those needed to convert pendant functionality serve only to degrade the polymer backbone. When IIR-g-vinyl ether was mixed with BMI and activated by 3.7 μmole/g of initiator, it cured rapidly and to a very high extent, reaching $\Delta G'$ = 281 kPa before reverting to a slightly lower modulus. By cutting the amount of initiator by half to a loading of 1.85 μmole/g DCP, the same cure extent was reached without incurring significant reversion. This behaviour is indicative of a very efficient reaction between vinyl ether and maleimide functionality, since only small amounts of peroxide are required to make full use of BMI. Note that the BMI increment was the highest observed in this work, reaching a ($\Delta G'_{DCP+BMI}$-$\Delta G'_{DCP}$) value of 247 (Table 3.1).

Further evidence of the reactivity of the vinyl ether-based system is provided by the cure yield generated by NPM. While this maleimide did not affect the cross-link density of IIR or our unsaturated co-curing materials appreciably, its influence on IIR-g-vinyl ether was pronounced, as it generated a

cross-link density of $\Delta G'$ = 183 kPa (Table 3.1). That a mono-functional reagent can affect such an efficient cure speaks to the efficiency of the alternating copolymerization between these functionalities. Moreover, this IIR-g-vinylether formulation contained 0.15 mmole vinyl ether and 0.075 mmole BMI per gram of polymer. This balance stoichiometry between co-curing and maleimide groups, coupled with the efficiency of their co-curing process, is likely to result in complete conversion of pendant vinyl ether, giving a thermoset that is free of residual unsaturation.

3.3.3 Co-curing Elastomer Properties

While time-resolved measurements of dynamic storage modulus are widely accepted indicators of elastomer cross-linking, thorough understanding of polymer properties requires knowledge of the material`s response to different deformation modes and time scales. Therefore, we have examined the mechanical properties of products derived from DCP+BMI cure formulations. The data presented in Figure 3.5 illustrate temperature sweeps of G' and tanδ, as well as static tensile and stress relaxation data.

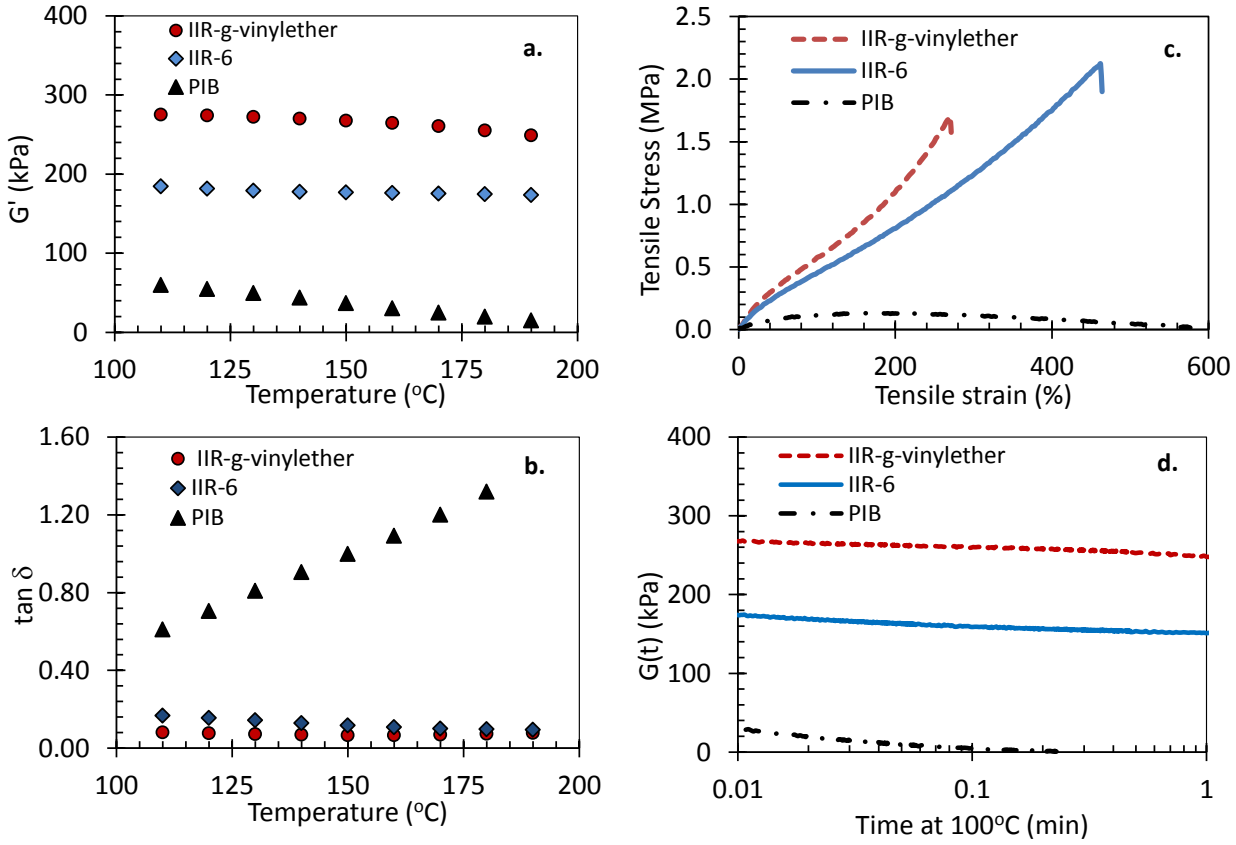


Figure 3.5 Physical properties of peroxide-cured elastomer formulations ([DCP]=3.70 μmole/g, [BMI] = 0.075 mmole/g, 160 °C cure temp); a G' at 1 Hz, 3° arc; b. tanδ at 1 Hz, 3° arc; c. tensile analysis at 25°C; d. stress relaxation at 100°C, 2° arc.

The dynamic rheological data presented in Figures 3.5a and 3.5b confirm that IIR-g-vinyl ether can be cross-linked to a greater extent by BMI+DCP than is possible for IIR-6 and PIB. Both co-curing elastomers showed consistent dynamic properties over the temperature range studied, with G' values maintaining near constant values throughout. The degradation incurred when PIB is treated with peroxide and coagent gave a low modulus material with comparatively low elasticity, as expected of an uncured elastomer.

The tensile data plotted in Figure 3.5c demonstrate the superior cross-link density within cured IIR-g-vinyl ether, as it provided higher 100% modulus and lower elongation at break than cured IIR-6. Of equal importance is the stability of this cross-link network`s response to a sustained strain. The stress

relaxation data provided in Figure 3.5d show that both co-cured elastomers maintain their static shear modulus, G(t) over our measurement period. This indicates that both materials are sufficiently cross-linked to resist relaxation under static deformation, and are therefore, suitable for applications involving such loads. However, further work is required to assess the long-term aging properties of these vulcanizates, since differences in their residual unsaturation may affect material performance.

3.4. Conclusions

Poly(isobutylene-co-isoprene) elastomers containing 2-6 mole% IP are unreactive to peroxide-only cure formulations, but cross-link with limited efficiency when combined with a bis-maleimide coagent. Co-curing elastomers bearing pendant polyether functionality provide higher cross-linking yields, owing to their reactivity in C-H bond addition to N-aryl maleimides. Similarly, sterically unencumbered, electron-rich olefin functionality can provide exceptional cross-linking rates and yields due to their ability to engage maleimides in alternating copolymerization.

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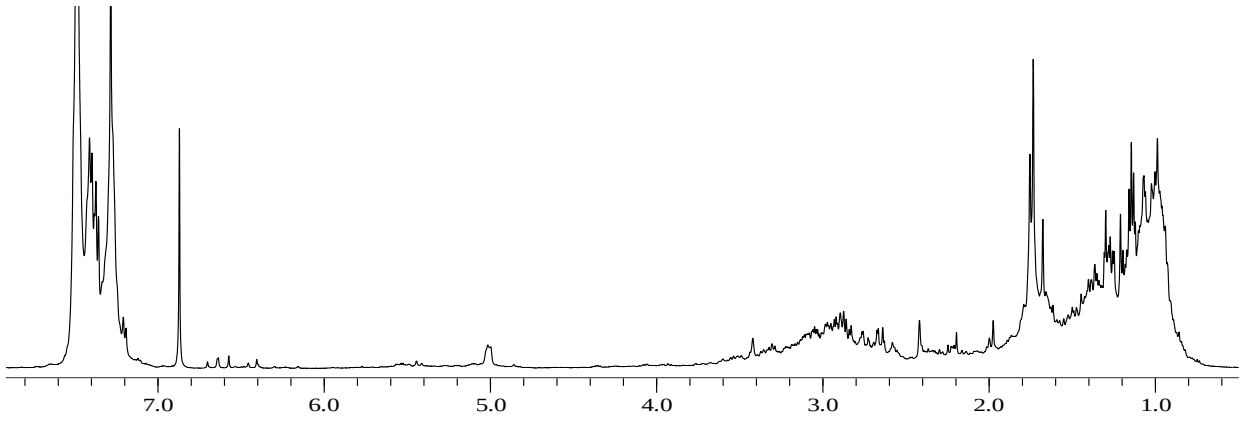
Supporting Information.

Dicumyl peroxide initiated reaction of 2-methyl-2-pentene and N-phenyl maleimide:
2-Methyl-2-pentene (1g, 11.8mmol), N-phenyl maleimide (0.2g, 1.18mmol) were mixed with dicumyl peroxide (0.001g, 3.6µmol) in anhydrous benzene solution (5g) and sealed within a 5mL stainless steel reactor. The reactor vessel was pressurized to 14 bar with nitrogen before being immersed in a silicone oil bath at 160°C under constant magnetic stirring. Benzene and residual 2-methyl-2-pentene were removed by Kugulrohr distillation (60°C; 0.03bar). ^{1}H NMR ($CDCl_3$) of the distillate is shown below. In addition to residual NPM, the spectrum shows the characteristic resonances of converted maleimide and substantial aliphatic resonances derived from converted 2-methyl-2-pentene. Resonances in the δ 4.5-6.0 ppm region are sparse, aside from a small signal at 5.02 ppm, indicating that the reaction product is predominately the saturated material expected of a copolymerization.



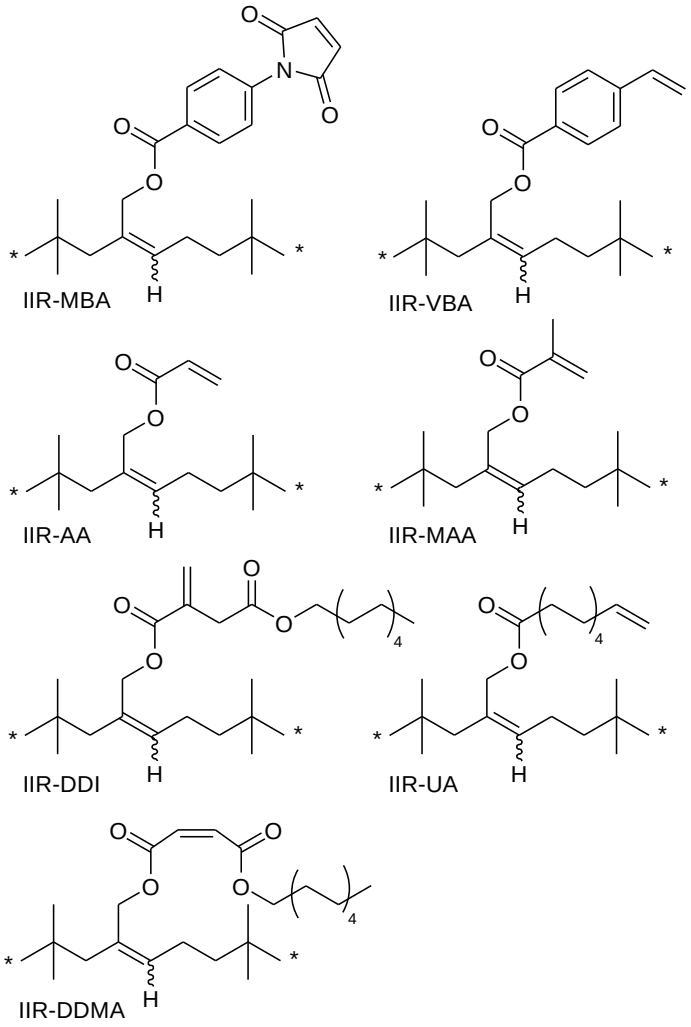
Chapter 4 : Reactivity/Stability relationships of IIR-derived Macromonomers

4.1 Introduction

The preceding chapter presented new chemistry for the radical cross-linking of isobutylene-rich elastomers, wherein pendant functionality was introduced to the polymer to render it reactive with respect to maleimide coagents. These co-curing elastomers were designed to be relatively stable at room temperature for prolonged periods, but highly reactive in combination with coagent. The most efficient co-curing functionality grafted to IIR included electron-rich olefins capable of alternating copolymerization with N-aryl maleimides. The thermosets derived from these copolymerizations can be free of residual unsaturation and, as such, may be expected to provide good long term stability while in service.

This chapter is concerned with multifunctional macromonomer derivatives in which the pendant groups introduced to the polymer backbone are capable of radical homopolymerization. This approach to preparing peroxide-curable IIR was first examined by researchers at Exxon, who prepared acrylate and methacrylate derivatives of brominated poly(isobutylene-co-paramethyl styrene), or BIMS.[1] Activation of pendant acrylate groups by peroxide thermolysis, UV-initiation, and electron beam bombardment gave highly cross-linked thermoset materials. More recently, Shude et al. studied acrylate and vinybenzoate ester derivatives of BIIR, which cured to high extent when treated with small amounts of dicumyl peroxide.[2] The primary deficiency of these multi-functional macromonomers is a lack of storage stability. When held at room temperature for several days, acrylate and styrenic functionalized materials cross-link to the gel point, rendering the elastomer unprocessible. The challenge in preparing a useful macromonomer is, therefore, to achieve high cross-linking activity in the absence of a coagent, while maintaining good thermo-oxidative stability.

This is a difficult task, since the most reactive monomers polymerize upon standing for prolonged periods, due to oxidative initiation. Less reactive monomers may provide the required stability, but may be unable to provide the cure activity needed to cross-link an IIR-based elastomer that is prone to radical degradation. Experimental data on the reactivity of different polymerizable functionality, both under peroxide-initiated and initiator-free conditions is required to determine whether a useful compromise can be obtained. The various functional groups examined in this work are illustrated in Scheme 4.1, and encompass highly reactive maleimide and styrenic moieties, as well as relatively unreactive α-olefin and maleate diesters. Dynamic storage modulus measurements made at 160°C are used to define the relative reactivity/stability of each material, with the intention of determining which functional group can provide the best compromise.



Scheme 4.1: IIR-derived macromonomers

Note that storage stability problems are not unique to macro-monomers, but exist for a wide range of elastomers, especially diene-based polymers containing high residual C=C contents.[3] These materials are typically stabilized using anti-oxidants such as hindered phenols, nitroxyls and/or peroxolytic reagents such as trialkylphosphites.[4] These additives intervene in polymer oxidation by serving as hydrogen atom donors in the place of the polymer, by trapping alkyl radicals as stable alkoxyamines, or by reducing hydroperoxide intermediates to their corresponding alcohols.[5,6] In the present case, long term storage stability of macro-monomer could be gained by selection of an appropriate additive. However, the potential commercial value of a macro-monomer lies in the cleanliness of its thermoset

derivative. Anti-oxidant residues that may be leached from the article are therefore undesirable. Furthermore, the presence of an antioxidant in a peroxide-cure formulation quenches initiator-derived radicals, thereby lowering the state of cure.[7] A new technology employing acrylated nitroxyls is examined in hope that this additive can provide the requisite storage stability without compromising peroxide cure yields or generating leachable by-products.

4.2 Experimental:

Materials: Acrylic acid (99%), vinylbenzoic acid (97%), methacrylic acid (99%), 10-undecenoic acid (98%), maleic anhydride (99%), 4-aminobenzoic acid (99%), sodium acetate (anhydrous, 99%), acetic anhydride (99%), itaconic anhydride (95%), dodecanol (95%), tetrabutylammonium bromide (98%), 4-hydroxy TEMPO (97)%, acryloyl chloride (97%), tetrabutylammoinium hydroxide (1M solution in methanol, 98%), dicumyl peroxide (98%), triethyl amine (99%), N,N'-m-phenylene maleimide (98%) were used as received from Sigma-aldrich.

Synthesis of IIR-g-methacrylate(IIR-MAA): Methacrylic acid (0.322 g, 3.7 mmol) was treated with a 1M solution of Bu_4NOH in methanol (3.7 ml, 3.7 mmol Bu_4NOH) to yield the desired Bu_4Ncarboxylate salt, which was isolated by removing methanol under vacuum. BIIR (11 g) and Bu_4NBr (0.53 g, 1.65 mmol) were dissolved in toluene (100 g) and heated to 85°C for 180 min. Bu_4Ncarboxylate salt (1.2g, 3.7 mmol) was added before heating the reaction mixture to 85°C for 60 min. The esterification product was isolated by precipitation from excess acetone, purified by dissolution/precipitation using hexanes/acetone, and dried under vacuum, yielding IIR-g-methacrylic acid. ^{1}H-NMR ($CDCl_3$): δ 6.03 (s,C**H$_2$**=C(CH_3)-COO-, 1H), δ 5.47 (s,C**H$_2$**=C(CH_3)-COO-,1H), δ 3.36 (s, (CH_2=C(C**H$_3$**)-COO-, 3H) ,δ 4.51 (E-ester, =CH-**CH$_2$**-OCO-, 2H, s), δ 4.56 (Z-ester, =CH-**CH$_2$**-OCO-, 2H, s).

Synthesis of IIR-*g*-maleimido benzoate (IIR-MBA): maleic anhydride (3 g, 0.03 mol) and 4-aminobenzoic acid (4.2 g, 0.03 mol) were dissolved in acetone (10 g) and the mixture was stirred for 12hrs at room temperature. The insoluble amidic acid precipitate was filtered off and dried in vacuum. The amidic acid (6 g, 0.025 mol) was treated with acetic anhydride (8 g, 0.078 mol) and sodium acetate (1g, 0.012mol) at 80°C for 15min. Maleimidobenzoic acid was isolated by precipitating through successive precipitation-dissolution in water/THF and dried in vacuum. ^{1}HNMR (DMSO-d_6): δ 7.21 (s,-C**H**=C**H**-, 2H), δ 7.50 (d, Ar-**H**, 2H), δ 8.02 (d, Ar-**H**, 2H). HR MS calculated for $C_{11}H_7NO_4$: 217.0371; found for $C_{11}H_7NO_4$: 217.0375. BIIR (10 g), Bu_4NBr (0.48 g, 1.5 mmol), maleimido benzoic acid (0.651 g, 3.0 mmol) and triethyl amine (0.3 g, 3.0 mmol) were dissolved in THF (100 g) and refluxed in a 250 ml vessel for 600 min. The esterification product was isolated by precipitation from excess acetone, purified by dissolution/precipitation using hexanes/acetone, and dried under vacuum, yielding IIR-g-maleimido-benzoate.

Synthesis of IIR-*g*-dodecyl itaconate (IIR-DDI): 1-Dodecanol (8.0 mmol,1.5 g) and itaconic anhydride (24 mmol, 2.7 g), were dissolved in toluene (10 g) and heated to 80°C for 4hr. Residual starting materials and solvent were removed by Kugelrohr distillation (T= 80°C, P=0.6 mmHg). The resulting acid-ester was isolated and dried. ^{1}HNMR (DMSO-d_6): δ 6.14 (d, HOOC-C**(=CH$_2$)**-CH_2-COO-, 1H), δ 5.74 (d, HOOC-C**(=CH$_2$)**-CH_2-COO-, 1H), δ 3.28 (s, HOOC-C**(=**CH_2**)**-C**H$_2$**-COO-, 1H) δ 3.98 (t, -CH_2-COO-C**H$_2$**-, 2H), δ 1.52 (m, -COO-CH_2-C**H$_2$**-, 2H), δ 1.36 (m, -COO-$(CH_2)_{10}$-C**H$_2$**-CH_3, 2H), δ 1.25 (m, -CH_2-(C**H$_2$**)$_9$- CH_2-CH_3, 18H), δ 0.87 (t, CH_2-C**H$_3$**, 3H). HR MS calculated for $C_{17}H_{31}O_4$ 299.2225; found for $C_{17}H_{31}O_4$: 299.2222.

Monododecyl itaconate (0.98 g, 3.3 mmol) was treated with a 1M solution of Bu_4NOH in methanol (3.3 ml, 3.3 mmol Bu_4NOH) to yield the desired Bu_4Ncarboxylate salt, which was isolated by removing methanol under vacuum. BIIR (11g) and Bu_4NBr (0.53 g, 1.65 mmol) were dissolved in toluene (100 g)

and heated to 85°C for 180 min. Bu_4Ncarboxylate salt (1.78 g, 3.3 mmol) was added before heating the reaction mixture to 85°C for 60 min. The esterification product was isolated by precipitation from excess acetone, purified by dissolution/precipitation using hexanes/acetone, and dried under vacuum, yielding IIR-g-dodecyl itaconate. ^{1}H-NMR ($CDCl_3$) : δ 6.24 (s, C**H$_2$**=C(CH_2)-COO-, 1H), δ 5.62 (s, C**H$_2$**=C(CH_2)-COO-, 1H), δ 3.36 (s, CH_2=C(C**H$_2$**)-COO-, 2H), δ 4.54 (E-ester, =CH-**CH$_2$**-OCO-, 2H, s), δ 4.60 (Z-ester, =CH-**CH$_2$**-OCO-, 2H, s).

Synthesis of IIR-g-undecenoate (IIR-UA) : 10-Undecenoic acid (0.88 g,3.7 mmol) was treated with a 1M solution of Bu_4NOH in methanol (4.8 ml, 4.8 mmol Bu_4NOH) to yield the desired Bu_4Ncarboxylate salt, which was isolated by removing methanol under vacuum. BIIR (16 g) and Bu_4NBr (0.77 g, 2.4 mmol) were dissolved in toluene (100 g) and heated to 85°C for 180 min. Bu_4Ncarboxylate salt (2.04 g, 4.8 mmol) was added before heating the reaction mixture to 85°C for 60 min. The esterification product was isolated by precipitation from excess acetone, purified by dissolution/precipitation using hexanes/acetone, and dried under vacuum, yielding IIR-g-undecenoate. ^{1}H-NMR ($CDCl_3$): δ 5.68 (m,-CH_2=C**H**-CH_2-, 1H), δ 4.85 (d, C**H$_2$**=CH-, 1H), δ 4.79 (d, C**H$_2$**=CH-, 1H), δ 4.51 (E-ester, =CH-**CH$_2$**-OCO-, 2H, s), δ 4.56 (Z-ester, =CH-**CH$_2$**-OCO-, 2H, s).

Synthesis of IIR-g-dodecyl maleate (IIR-DDMA): 1-Dodecanol (1.5 g, 8.04 mmol) and maleic anhydride (0.98 g, 10 mmol) were dissolved in toluene (10 g) and heated to 80°C for 4hr. Residual starting materials and solvent were removed by Kugelrohr distillation (T= 80°C, P=0.6mmHg). The resulting acid-ester was isolated. ^{1}HNMR ($CDCl_3$): δ 6.46 (d, HOOC-C**H**=CH-COO-, 1H), δ 6.36 (d, HOOC-CH=C**H**-COO-, 1H), δ 4.27 (t, =CH-COO-C**H$_2$**-, 2H), δ 1.71 (m, -COO-CH_2-C**H$_2$**-, 2H), δ 1.36 (m, -COO-$(CH_2)_{10}$-C**H$_2$**-CH_3, 2H), δ 1.25 (m, -CH_2-(C**H$_2$**)$_9$- CH_2-CH_3, 18H), δ 0.87 (t, CH_2-C**H$_3$**, 3H). HR MS calculated for $C_{16}H_{29}O_4$ 285.2078; found for $C_{16}H_{29}O_4$: 285.2065.

Monododecyl maleate (0.94 g, 3.3 mmol) was treated with a 1M solution of Bu_4NOH in methanol (3.3ml, 3.3 mmol Bu_4NOH) to yield the desired Bu_4Ncarboxylate salt, which was isolated by removing methanol under vacuum.BIIR (11 g) and Bu_4NBr (0.53 g, 1.6 mmol) were dissolved in toluene (100g) and heated to 85°C for 180 min. Bu_4Ncarboxylate salt (1.7 g, 3.3 mmol) was added before heating the reaction mixture to 85°C for 60 min. The esterification product was isolated by precipitation from excess acetone, purified by dissolution/precipitation using hexanes/acetone, and dried under vacuum, yielding IIR-g-dodecyl maleate. ^{1}H-NMR ($CDCl_3$) : δ 6.19 (s, OOC-C**H**=C**H**-COO-, 2H), δ 4.11 (t, -CH_2-CH_2-COO-C**H_2**-, 2H), δ 4.58 (E-ester, =CH-**CH_2**-OCO-, 2H, s), δ 4.66 (Z-ester, =CH-**CH_2**-OCO-, 2H, s).

Synthesis of IIR-g-vinylbenzoate (IIR-VBA): 4-vinylbenzoic acid (0.44 g, 3.0 mmol) was treated with a 1M solution of Bu_4NOH in methanol (3.0 ml, 3.0 mmol Bu_4NOH) to yield the desired Bu_4Ncarboxylate salt, which was isolated by removing methanol under vacuum. BIIR (10g) and Bu_4NBr (0.77 g, 2.4 mmol) were dissolved in toluene (100g) and heated to 85°C for 180 min. Bu_4Ncarboxylate salt (1.16 g, 3.0 mmol) was added before heating the reaction mixture to 85°C for 60 min. The esterification product was isolated by precipitation from excess acetone, purified by dissolution/precipitation using hexanes/acetone, and dried under vacuum, yielding IIR-g-vinylbenzoate. ^{1}H-NMR ($CDCl_3$): δ 6.73 (dd,-CH_2=C**H**-Ar, 1H), δ 5.82 (dd, C**H_2**=CH-, 1H), δ 5.48 (dd, C**H_2**=CH-, 1H), δ 4.78 (E-ester, =CH-**CH_2**-OCO-, 2H, s), δ 4.81 (Z-ester, =CH-**CH_2**-OCO-, 2H, s).

Synthesis of IIR-g-acrylate (IIR-AA): Acrylic acid (0.21 g, 3.0 mmol) was treated with a 1M solution of Bu_4NOH in methanol (3.0 ml, 3.0 mmol Bu_4NOH) to yield the desired Bu_4Ncarboxylate salt, which was isolated by removing methanol under vacuum. BIIR (10g) and Bu_4NBr (0.48 g, 1.5 mmol) were dissolved in toluene (100g) and heated to 85°C for 180 min. Bu_4Ncarboxylate salt (0.94 g, 3.0 mmol) was added

before heating the reaction mixture to 85°C for 60 min. The esterification product was isolated by precipitation from excess acetone, purified by dissolution/precipitation using hexanes/acetone, and dried under vacuum, yielding IIR-g-acrylate. ^{1}H-NMR ($CDCl_3$): δ 6.12 (dd, CH_2=C**H**-COO-, 1H), δ 6.40 (dd, C**H$_2$**=CH-, 1H), δ 5.82 (dd, C**H$_2$**=CH-, 1H), δ 4.66 (E-ester, =CH-COO-**CH$_2$**-, 2H, s), δ 4.60 (Z-ester, =CH-COO-**CH$_2$**-, 2H, s).

Synthesis of 4-Acryloyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl: A solution of TEMPOH (1 g, 5.8 mmol) and triethyl amine (706 mg, 0.97 mL, 6.9 mmol) was reacted with acryloyl chloride (0.632 g, 0.57 mL, 6.9 mmol) in toluene at room temperature for 16 hours. The solids were removed by filtration and washed multiple times with toluene. The solution was dried under vacuum to yield orange crystals. Crystals were recrystallized from cyclohexane and dried under air flow. m.p. 92°C. ^{1}H-NMR: ($CDCl_3$): δ (ppm), δ 6.49 (1 H, dd, HC=C), δ 6.19 (1 H, dd, C=CH-C), δ 5.96 (1 H, dd, HC=C), 1.0 – 2.0 (17 H). High-res. M.S. $C_{12}H_{20}NO_3$ calculated m/z $[M+2H]^+$ 228.1596; found m/z 228.1599.

Instrumentation and Analysis: ^{1}H-NMR spectra were acquired in $CDCl_3$ on a Bruker Avance-600 spectrometer. Mass spectra were obtained on an Applied Biosystems QStar XL QqTOF mass spectrometer. Dynamic shear modulus measurements were recorded using an Alpha Technologies, Advanced Polymer Analyzer 2000. Pressed samples of elastomer were coated with the required amount of a stock solution of DCP in acetone, and allowed to dry prior to passing three times through a 2-roll mill. This mixed compound was cured in the rheometer cavity at 3° oscillation arc and a frequency of 1 Hz.

4.3 Results and Discussion

4.3.1. Peroxide-initiated cross-linking dynamics and yields

The multi-functional macromonomers depicted in Scheme 4.1 were prepared by nucleophilic displacement of bromide from BIIR by the required carboxylate salt. These syntheses involved the pre-isomerization of the exo-allylic bromide functionality within the starting material to E,Z-BrMe isomers by reaction with Bu_4NBr. This was done to generate a more reactive electrophile, thereby increasing esterification rates[8] and limiting the time that potentially sensitive macro-monomer functional groups would be maintained in solution at elevated temperature. The desired esters were produced in quantitative yield without complications associated with dehydrohalogenation. As a result, all materials contained 0.15 mmoles of reactive functionality per gram of elastomer, distributed randomly within each polymer chain. Assuming a number average molecular weight of 250,000 g/mole for the starting material, 0.15 mmole/g corresponds to about 40 functional groups per polymer chain, with an average molecular weight between functional groups on the order of 6000 g/mole.

The macro-monomer functionality examined in this study encompassed a wide range of free radical polymerization activity. Acrylic and styrenic monomers are polymerized with high kinetic chain lengths at temperatures far lower than those used in commercial vulcanization processes.[9,10] Therefore, the expectation was that IIR-VBA and IIR-AA would be very reactive at 160°C, despite the low active C=C concentration in these polymers. Similarly, the N-arylmaleimide functionality within IIR-MBA is expected to be reactive, given the efficiency of maleimide coagents demonstrated in previous chapters. The undeceneoate ester (IIR-UA) lies at the opposite end of the reactivity scale, owing to low intrinsic rates of radical addition, and degradative chain transfer by allylic hydrogen atom abstraction. The remaining C=C functionalities, IIR-DDMA, IIR-MMA and IIR-DDI can be polymerized to varying degrees,

with maleate diesters being much less reactive than methacrylates and their structural analogues, itaconate diesters.

While knowledge of the kinetic chain length of monomer polymerization is helpful in deciding which functionality to include in this study, it is not sufficient to predict macro-monomer reactivity. The cross-linking reactions of present interest involve low concentrations of polymer-bound monomer, which are activated at temperatures well in excess of conventional polymerizations. As such, experimental data of the type presented in Figure 4.1 are required to assess macro-monomer performance. In this plot, the evolution of the material's dynamic storage modulus (G') is presented for each macro-monomer when mixed with 18 μmole of DCP per gram of polymer and heated to 160°C. An efficient macro-monomer is one that converts its 0.15 mmole/g of macromonomer functionality into a covalent polymer network of high storage modulus. An ideal cure rate depends somewhat on the manufacturing process, but in general a high cross-linking rate at 160°C is desirable, as long as the material does not cure while the polymer is mixed with other additives during compounding.

The categorization of macro-monomers based on the polymerizability of their functionality is generally consistent with their cure activity, with IIR-VBA demonstrating the highest cross-linking rate and yield of all the materials tested. A maximum storage modulus of 440 kPa was observed for the IIR-VBA + DCP formulation after 5 min at 160°C, after which it declined to 392 kPa at the 20 min mark. This cure reversion is an undesirable consequence of the susceptibility of butyl rubber to radical degradation. As discussed previously, IIR does not cure under the action of peroxides, but loses molecular weight to β-scission of alkyl macro-radical intermediates. The net loss in G' observed for IIR-VBA and IIR-MBA occurs when macro-monomer conversion to cross-links is no longer competitive with polymer backbone

degradation. This shift is likely the result of complete consumption of pendant monomer groups, leaving chain scission as the principal reaction that affects polymer molecular weight.

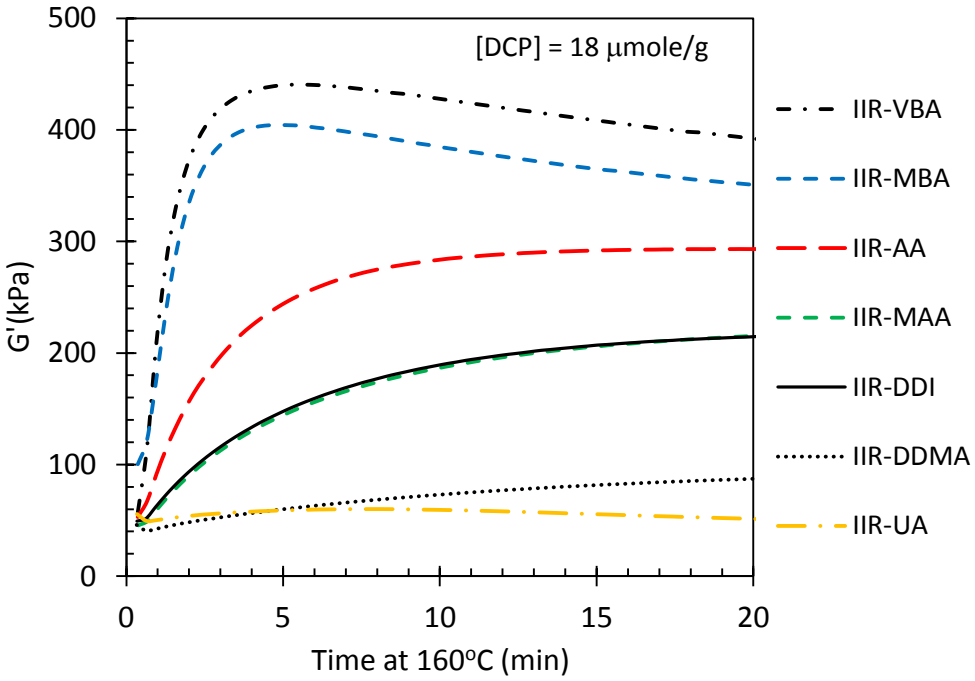


Figure 4.1: Dynamics of peroxide-initiated macro-monomer cross-linking ([DCP] = 18 µmol/g).

The cure rate and extent provided by IIR-AA was more moderate, as G' reached a plateau of 293 kPa after 20 minutes at 160°C. Note that the half-life of DCP at this temperature is 5.4 min, meaning that over 90% of the peroxide has decomposed at this point in the process. As expected, the reactivity of IIR-MAA and IIR-DDI was very similar, and considerably less than the unsubstituted acrylate functionality within IIR-AA. IIR-DDMA and IIR-UA proved incapable of generating appreciable cross-linking activity.

A closer examination of the cure dynamics data in Figure 4.1 reveals a relationship between the cross-link density provided by a macro-monomer, as measured by the difference in storage modulus ($\Delta G' = G'_{max} - G'_{min}$), and the maximum rate of cross-linking ($dG'/dt\,|_{max}$). The latter is determined by taking the numerical derivative of the G' versus time data, and reporting the highest rate observed throughout the curing reaction. Figure 4.2 presents a semi-log plot of $\Delta G'$ against $dG'/dt\,|_{max}$ for each macro-monomer,

showing the clear dependence on macro-monomer cure reactivity and overall cross-linking extent. Even though all the macro-monomers contained 0.15 mmoles of reactive functionality per gram of polymer, and therefore had the same potential to effect cross-linking, the styrenic material gave an exceptional final modulus, while the maleate diester generated a meagre cross-link density.

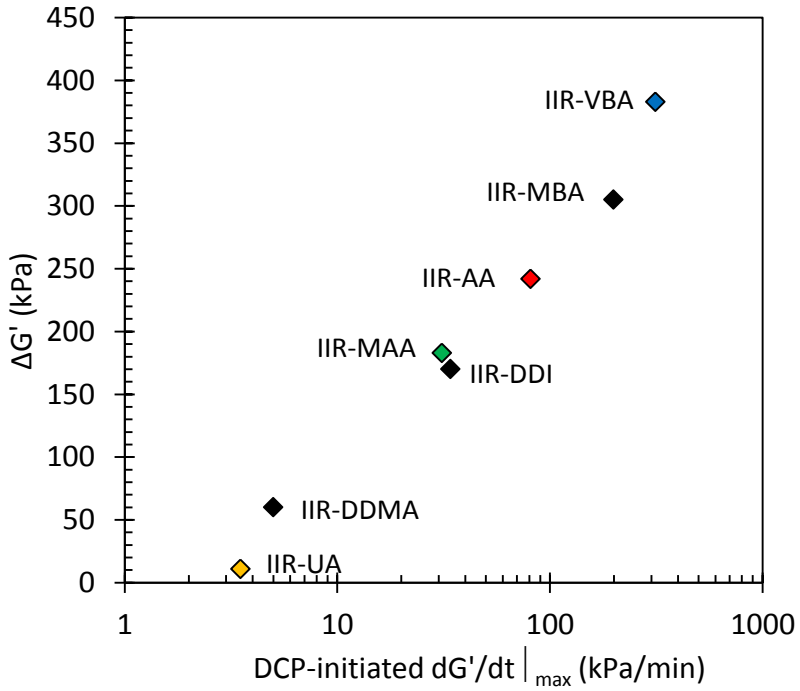


Figure 4.2: Cure yield versus maximum cure rate of peroxide-initiated macro-monomer cross-linking ([DCP] = 18 µmole/g; T = 160°C; t = 60 min).

There are two reasons for the relatively poor performance of the less reactive materials. The first underlying cause is a competition between macro-monomer cross-linking and polymer backbone degradation. Note that the activation of a macro-monomer by peroxide initiates cross-linking as well as chain scission. Figure 4.3 provides storage modulus data for poly(isobutylene-co-isoprene) (IIR) compounded with DCP and various unbound monomers. Note that IIR contains no pendant macro-monomer functionality, and the material degraded when treated with peroxide alone. More importantly, the presence of styrene, butyl acrylate, butyl methacrylate or N-phenyl maleimide did not prevent IIR degradation. By extension, the polymerizable functionality that is bound to the

corresponding macro-monomers does not eliminate backbone degradation. It is the relative balance of cross-linking and scission that dictates cross-linking rates and yields of macro-monomer cure formulations.

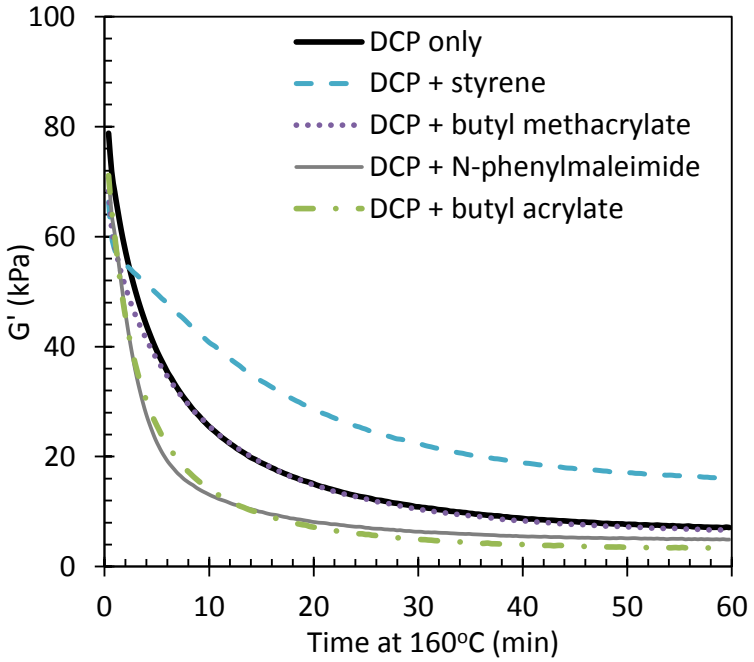


Figure 4.3: Dynamics of IIR degradation in the presence of unbound monomers ([DCP] = 18 µmol/g; [monomer] = 0.15 mmole/g).

However, this is not a simple competition between two independent reactions. If polymer degradation scission is favoured, then it will generate small chain fragments whose low molecular weight makes them more difficult to bring up to, and beyond, the gel point. No matter how much initiator is charged to an inactive macro-monomer, it may never produce a tightly cross-linked thermoset. Conversely, if cross-linking is favoured, then it will generate highly branched architectures whose molecular weight is less sensitive to chain scission than linear parent materials. Reactive macro-monomers quickly establish a polymer network that is resistant to degradation. Therefore a material such as IIR-VBA can generate a high storage modulus at the 5 min mark of a DCP cure, yielding a covalent network that resists large-

scale degradation over the next 15 min, even though over 50% of the peroxide remains active (Figure 4.1).

Incomplete monomer conversion is a second potential cause of poor macro-monomer performance. Consider the cure dynamics observed for the methacrylate-based macro-monomer, IIR-MMA (Figure 4.4). It is clear that network growth is favoured over chain scission for this system, as the storage modulus increased throughout the 20 min duration of the experiment, regardless of the initiator loading used. However, IIR-MAA responded continuously to increases in DCP concentration as they were raised from 3.6μmole/g to 36μmole/g, at which point cure reversion was observed. This is indicative of near complete methacrylate consumption, and it indicates that IIR-MAA requires more initiator to realize its full cross-linking potential than is needed for more reactive macro-monomers such as IIR-VBA. Note, however, that even when IIR-MAA is supplied with sufficient peroxide, it cannot match the more reactive macro-monomers, due to its weaker competitive advantage of cross-linking over chain scission.

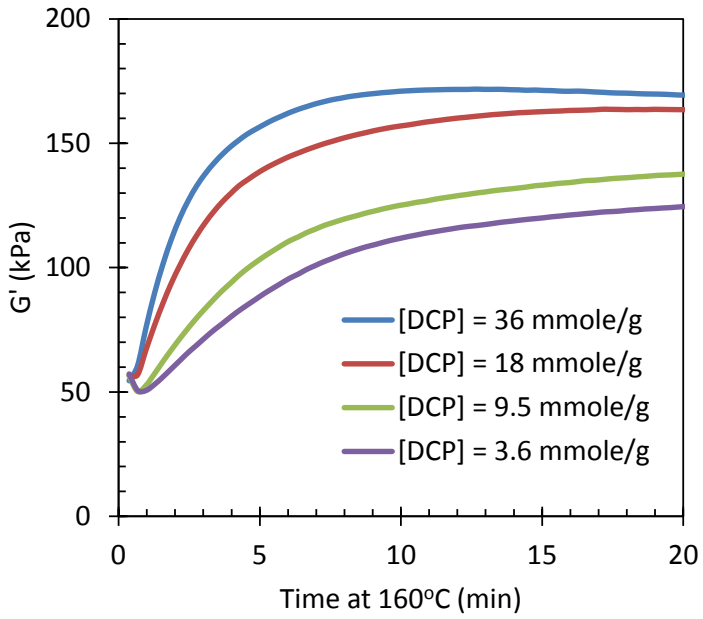


Figure 4.4: Dynamics of peroxide-initiated IIR-MMA cross-linking at different DCP concentrations.

4.3.2. Macro-monomer stability

Although macro-monomer cure yields and rates are important, all elastomers must remain processable during conventional rubber processing operations. This includes the mixing of the polymer with various fillers, colourants, cure-initiators and other additives, as well as forming of the resulting compound into the desired shape. This requires a macro-monomer to be stable with respect to radical initiation by non-peroxide sources, which include oxidative initiation, mechanical initiation during high-shear mixing, thermolysis of weak C-H and C-C bonds, and even the spontaneous auto-initiation behaviour observed for some maleimide monomers. Therefore, this study of macro-monomer reactivity turned to examination of the intrinsic stability of these polymers when heated to 160°C in the absence of peroxide initiator. The results of these cure rheology studies are presented in Figure 4.5.

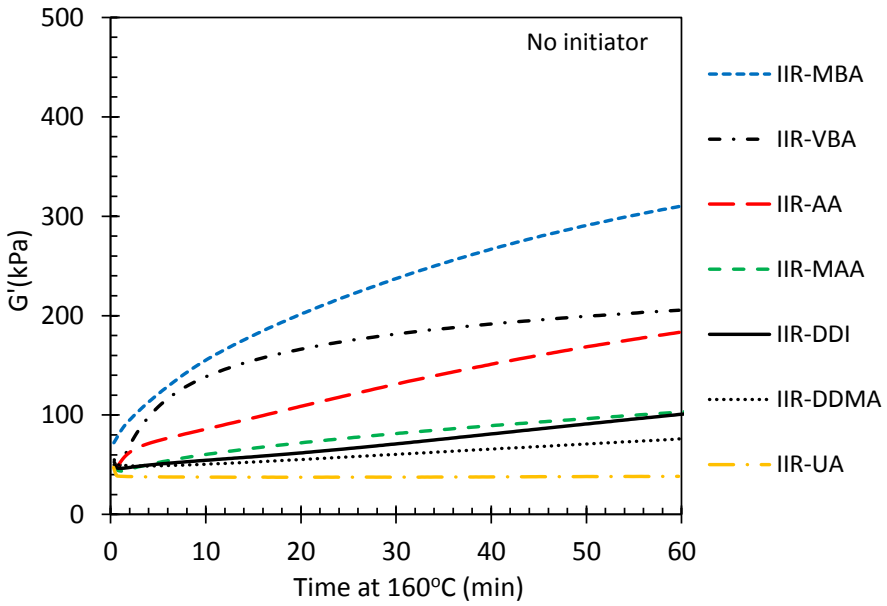


Figure 4.5 Dynamics of auto-initiated macro-monomer cross-linking ([DCP] = 0 µmol/g).

Over a 60 min period at 160°C, IIR-UA was the only macro-monomer that was completely stable. The maleate ester, IIR-DDMA, was substantially inert, while the methacrylate and itaconate esters provided

comparable stability. Of the seven materials tested only three polymers, IIR-AA, IIR-VBA and IIR-MBA, would be considered too unstable to satisfy commercial storage, compounding, and shaping process requirements. Taking the time derivative of the uninitiated cross-linking data provided $dG'/dt\big|_{max}$, a quantitative measure of macro-monomer instability, which could then be plotted against the rate of DCP-initiated cure activity, as shown in Figure 4.6. On such a plot, an ideal macro-monomer resides in the bottom right hand corner, since such a material would be exceptionally stable, except when activated by a radical initiator, whereupon it would provide good cure rates and cross-link yields.

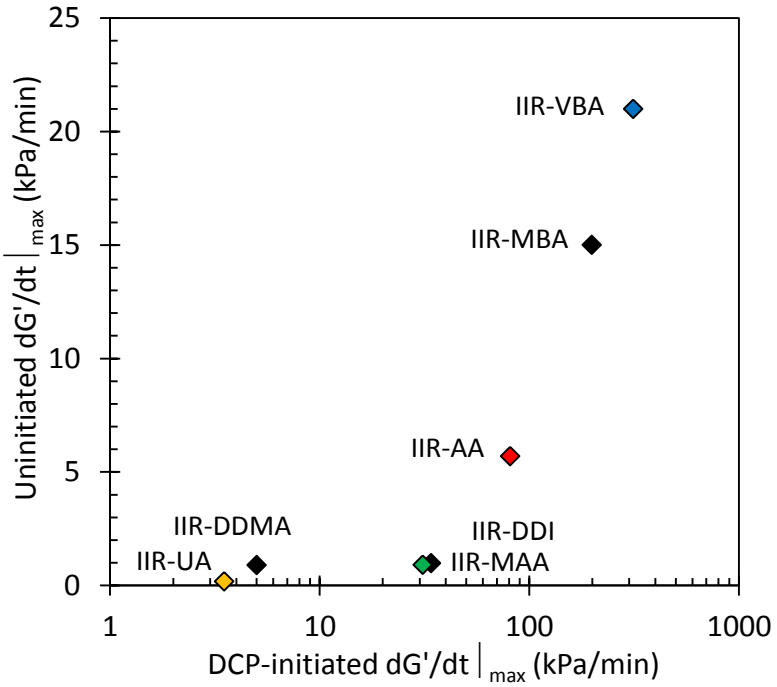
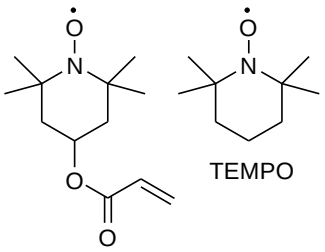


Figure 4.6: Cure yield versus maximum cure rate of peroxide-initiated macro-monomer cross-linking (T = 160°C; t = 60 min).

It is clear from this plot that the most favourable balance between cure activity and stability is afforded by the 2-alkyl substituted acrylates, IIR-MAA and IIR-DDI. Therefore, if all additives are to be avoided, including anti-oxidants and cure-boosting coagents, then these macro-monomers offer the best compromise. Indeed, these materials can be stored at room temperature without stabilizers for several

months without cross-linking, whereas acrylate, maleimide and vinylbenzoate macro-monomers can reach the gel point in a matter of days.

As noted above, the standard approach to mitigating polymer instability is to apply anti-oxidants in an effort to quench radical activity and, by extension, limit the extent of macro-monomer oligomerization. This approach has unfortunate consequences. In the first place, conventional anti-oxidants reduce the yield of peroxide-initiated cross-linking, thereby requiring the use of higher initiator levels to overcome cross-link density losses.[4] Secondly, antioxidants introduce volatile organic compounds to the thermoset product that are undesirable where clean-curing materials are required, such as in pharmaceutical and packaging applications. In effort to make the more reactive macro-monomers acceptable for commercial development, a functional nitroxyl (AOTEMPO, Scheme 4.2) was evaluated as a stabilizing additive that does not compromise cure yields, nor introduce leachable by-products.



Scheme 4.2: Nitroxyl based radical traps

Nitroxyls are used widely as carbon-centred radical traps, quenching radical activity by combination to yield spin-paired alkoxyamines.[5] They react at the diffusion limit of bimolecular reaction velocity, with rate constants on the order of 10^8-10^9 $M^{-1}s^{1}$,[11] and do not trap oxyen-centred radicals such as the cumyloxyl intermediates derived from DCP thermolysis. Nitroxyls such as TEMPO have found recent application in controlled radical polymerization chemistry, wherein the reversibility of alkoxyamine formation is used to induce pseudo-living polymerization of acrylate and styrenic monomers. In the

present context, reversible trapping of macro-radicals is not particularly desirable. The objective is to provide stability to the macro-monomer during long-term storage at room temperature, and during polymer compounding operations that routinely reach temperatures above 100°C.

Another potential benefit from the use of AOTEMPO concerns cross-linking activity in the early stages of the peroxide-initiated process. It is frequently desired to delay the onset of an elastomer cure to allow the compound to assume the shape of the mould. Given the exceptional activity of macro-monomers such as IIR-VBA, delayed-onset cross-linking may be highly beneficial, especially if it can be gained without compromising cure yields and generating volatile by-products. It is the latter concern that motivates the use of a functional nitroxyl such as AOTEMPO, as opposed to a simpler analogue such as TEMPO. Since the quenching of macro-radicals by combination with nitroxyl reduces the amount of peroxide-derived radicals that can initiate cross-linking, it stands to reason that introducing additional acrylate functionality as an AOTEMPO-based alkoxyamine will help to recover potential storage modulus losses. Furthermore, alkoxyamines that are not attached to the polymer, such as those generated by methyl radical trapping, have the potential to engage macro-monomer functionality in copolymerization, thereby rendering them polymer bound.

The data plotted in Figure 4.7 illustrate cure dynamics observed for a range of IIR-AA formulations. Using peroxide alone produced rapid cross-linking in the earliest stages of the process, when the concentrations of initiator and macro-monomer functionality were greatest. The maximum storage modulus was recorded at the 10 min mark of the cure (roughly two half-lives of DCP at 160°C), at which point significant cure reversion was observed due to backbone degradation. The inclusion of AOTEMPO in the peroxide cure formulation produced many of the process improvements described above. Initial cross-linking rates were depressed strongly, but not completely as is observed for unmodified

polyolefins such as linear low density polyethylene.[12] An induction time of approximately 5 minutes was provided by the trapping of alkyl radicals by nitroxyl functionality, and was followed by a rapid and efficient cure to a high final modulus. As such, AOTEMPO has been proven capable of providing scorch protection to macro-monomer cures without severely compromising cross-link density.

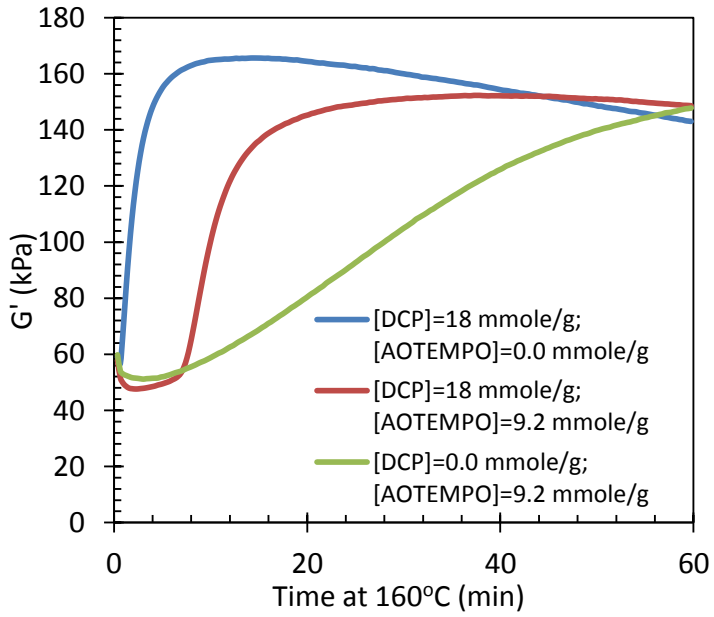


Figure 4.7: Reactivity of IIR-AA in various DCP and AOTEMPO formulations.

Of particular interest is the behaviour of the IIR-AA + AOTEMPO mixture containing no peroxide. This initiator-free composition cured slowly but continuously throughout the experiment, even though a significant amount of nitroxyl was present. Since AOTEMPO quenched radical activity in the DCP-initiated formulation, it is clear that the nitroxyl can mitigate free radical oligomerization of macro-monomer functionality. Nevertheless, the antioxidant could not stop IIR-AA from auto-initiating. This suggests that non-radical oligomerization pathways may be important contributors to macro-monomer instability. Of the potential options, anionic polymerization through enolate intermediates is the most likely.

It is well known that styrenic, acrylic and maleimide monomers are susceptible to nucleophilic addition, and under appropriate reaction conditions, they can be polymerized to high molecular weight.[13,14] Although the conditions under which the macro-monomers of current interest are very different, the possibility exists for anionic oligomerization to bring about the cross-linking extents observed in this work. Preliminary evidence of this mechanism was gained by mixing IIR-AA with tetrabutylammonium acetate (Bu_4NOAc) and heating to 160°C. If a conjugate addition process is capable of curing -linking the macro-monomer, then the presence of a good nucleophile is expected to initiate cross-linking. The data presented in Figure 4.8 demonstrate significant curing activity, suggesting that IIR-AA is susceptible to cure-initiation by a conjugate addition mechanism.

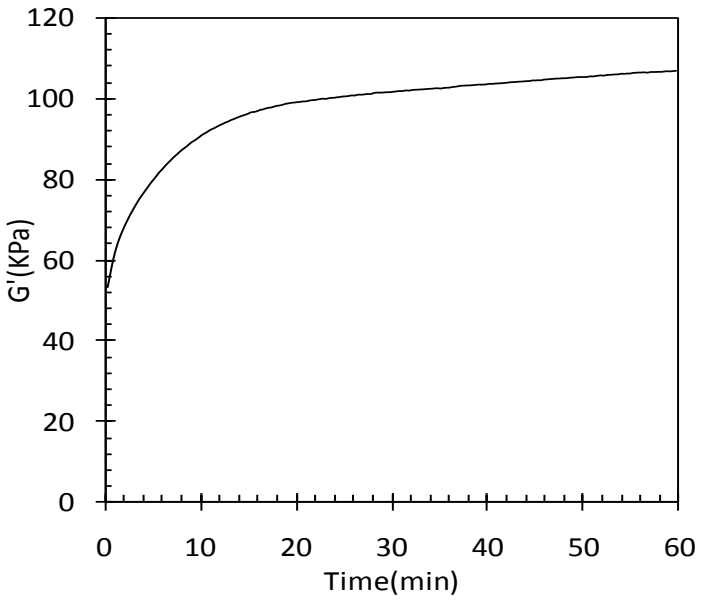


Figure 4.8 Cross-linking dynamics of an IIR-AA + Bu_4NOAc (16µmol/g) mixture.

This discovery raises several questions concerning macro-monomer technology. It is unclear whether reactive macro-monomers can, in fact, be stabilized against the apparent auto-initiation observed throughout this work. Rigorous purification to remove residual carboxylates charged to BIIR modification reactions, and indeed to IIR halogenation processes might improve macro-monomer stability, as could the addition of an organic acid whose conjugate base is non-nuclephilic (e.g. toluene sulfonic acid). An anionic cure process may also be put to some practical use, since it could proceed

without degrading the polymer backbone. Whereas, peroxide-initiated macro-monomer cures involve simultaneous molecular weight growth and loss, an anionic process might reach higher cross-link densities.

4.4 Conclusions

Whereas commercial grades of isobutylene-rich elastomers do not cure under the action of peroxides, macro-monomers bearing oligomerizable C=C functionality can be cured to high extent. These materials undergo simultaneous cross-linking and degradation when activated by radical initiators, with the competitive balance dictated by the reactivity of the oligomerizable group. Highly reactive maleimide, styrenic and acrylate functionality provides good peroxide cure activity at the expense of storage and compounding stability, while less reactive maleate esters and unactivated vinyl groups provide good stability at the expense of peroxide cure extent. Surprisingly, nitroxyls can mitigate free radical cure activity, but do not prevent auto-initiation, and further work is required to elucidate the source of macro-monomer instability.

4.5. References

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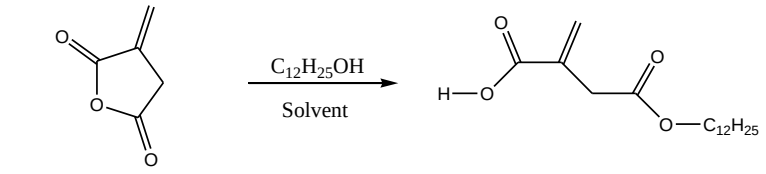
Chapter 5 : Design, Synthesis and Characterization of IIR-derived Functional Macromonomers

5.1. Introduction:

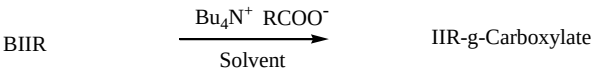
In the last chapter, the scope of the macromonomer approach to prepare peroxide curable butyl rubber derivatives was discussed. The essence of the macromonomers is their reactivity when activated by peroxide induced free radicals, balanced by their stability towards auto-polymerization during the shelf-life. On one end of the spectrum were highly reactive functional groups like vinyl benzoate, maleimido benzoate and acrylate. Macromonomers based on these functional groups had high rate of cure and cure yields when treated with peroxides at high temperatures. Their high reactivity, although of great use during curing, made them unstable even in the absence of peroxides as they exhibited significant auto-polymerization tendencies. On the other hand, the macromonomers containing undecenoate and dodecyl maleate offered highly stable derivatives but were hampered by low yields and cure rates.

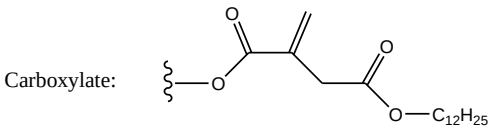
On the balance of their propensity to homo-polymerize and their stability towards auto-polymerization at high temperatures, macromonomers containing methacrylate and dodecyl itaconate are of interest. Particularly, IIR-g-dodecyl itaconate is of great importance because of its chemical structure. Its similarity to methacrylate in chemical structure and reactivity were reflected in the cure rates and yields. However, in addition to the reactive itaconate site, the molecule also has another site taken up by dodecyl group in IIR-g-dodecyl itaconate (IIR-g-ITA(C_{12}). This site provides a platform upon which various additional functional groups can be incorporated in addition to the itaconate groups. BIIR, which is the precursor for preparing derivatives of butyl rubber, poses an upper limit to the amount of functionality that can be incorporated (~0.15mmol/g). As a result different functional groups cannot be incorporated without compromising the concentration of the each of the functional groups in the polymer. But, this can be overcome by taking advantage of the bi-functional itaconate based nucleophiles.

Ring opening itaconic anhydride by functional alcohols yields functional half-esters.[1] This can then be used in the nucleophilic substitution reactions on BIIR to prepare "functional macromonomers." In this chapter, this pathway is exploited to create several functional macromonomers of butyl rubber (Scheme 5.1). Each of these derivatives was tailor made to achieve specific objectives and their properties will be demonstrated individually.

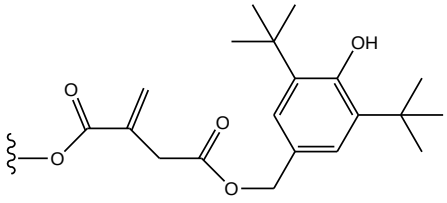


Itaconic Anhydride

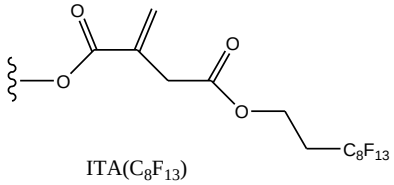




ITA(C_{12})



ITA(BHT)



ITA(C_8F_{13})

Scheme 5.1: Chemical modification of BIIR with itaconate half-esters.

5.2. Experimental

Materials: BIIR (LANXESS Bromobutyl 2030, allylic bromide content ~0.15 mmol/ g) was provided by LANXESS Inc. (Sarnia, ON). 1-dodecanol (95%), itaconic anhydride (95%), tetrabutylammonium bromide (98%), tetrabutylammonium hydroxide (1M solution in methanol, 98%), dicumyl peroxide (98%), 3,5-Di-tert-butyl-4-hydroxybenzyl alcohol (99%), 1H,1H,2H,2H-Perfluoro-1-octanol (98%), succinic anhydride (97%), sodium hydroxide, zinc oxide (99%) were used as received from Sigma Aldrich.

Synthesis of IIR-g-dodecyl itaconate: 1-Dodecanol (8.0mmol,1.5g) and itaconic anhydride (24 mmol, 2.7 g), were dissolved in toluene (10g) and heated to 80°C for 4hr. Residual starting materials and solvent were removed by Kugelrohr distillation (T= 80°C, P=0.6mmHg). The resulting acid-ester was isolated and dried. ^{1}HNMR (DMSO-d_6): δ 6.12.6.14 (d, HOOC-C**(=CH$_2$)**-CH_2-COO-, 1H), δ 5.74-5.76 (d, HOOC-C**(=CH$_2$)**-CH_2-COO-, 1H), δ 3.28 (s, HOOC-C(=CH_2)-C**H$_2$**-COO-, 1H), δ 3.97-3.99 (t, -CH_2-COO-C**H$_2$**-, 2H), δ 1.51-1.53 (m, -COO-CH_2-C**H$_2$**-, 2H), δ 1.36-1.38 (m, -COO-$(CH_2)_{10}$-C**H$_2$**-CH_3, 2H), δ 1.23-1.29 (m, -CH_2-(C**H$_2$**)$_9$- CH_2-CH_3, 18H), δ 0.85-0.99 (t, CH_2-C**H$_3$**, 3H). HR MS calculated for $C_{17}H_{31}O_4$ 299.2225; found for $C_{17}H_{31}O_4$: 299.2222. M.P: 71-73°C.

Monododecyl itaconate (0.98 g, 3.3mmol) was treated with a 1M solution of Bu_4NOH in methanol (3.3ml, 3.3mmol Bu_4NOH) to yield the desired Bu_4Ncarboxylate salt, which was isolated by removing methanol under vacuum. BIIR (11g) and Bu_4NBr (0.53 g, 1.65mmol) were dissolved in toluene (100g) and heated to 85°C for 180 min. Bu_4Ncarboxylate salt (1.78g, 3.3mmol) was added before heating the reaction mixture to 85°C for 60 min. The esterification product was isolated by precipitation from excess acetone, purified by dissolution/precipitation using hexanes/acetone, and dried under vacuum, yielding IIR-g-dodecyl itaconate. ^{1}H-NMR ($CDCl_3$) : δ 6.24 (s, C**H$_2$**=C(CH_2)-COO-, 1H), δ 5.62 (s, C**H$_2$**=C(CH_2)-

COO-, 1H), δ 3.36 (s, CH_2=C(C**H_2**)-COO-, 2H), δ 4.54 (E-ester, =CH-**CH_2**-OCO-, 2H, s), δ 4.60 (Z-ester, =CH-**CH_2**-OCO-, 2H, s).

Synthesis of IIR-g-BHT itaconate

3,5-Di-tert-butyl-4-hydroxybenzyl alcohol (3.9mmol, 0.95g) and itaconic anhydride (5.0 mmol, 0.6 g), were dissolved in toluene (10 g) and heated to 80°C for 4hr. Residual starting materials and solvent were removed by Kugulrohr distillation (T= 80°C, P=0.6 mmHg). The resulting acid-ester was isolated and dried. ^{1}HNMR ($CDCl_3$): δ 7.03 (s, Ar-**H**, 2H) δ 6.44 (s, HOOC-C**(=CH_2)**-CH_2-COO-, 1H), δ 5.81 (s, HOOC-C**(=CH_2)**-CH_2-COO-, 1H), δ 3.31 (s, HOOC-C(=CH_2)-C**H_2**-COO-, 1H), δ 5.02 (s, Ar-O**H**, 1H) , δ 5.24 (s, Ar-C**H_2**-O-CO-, 2H), δ 1.40 (s, Ar-(C(C**H_3**)$_3$)$_2$, 18H). HR MS calculated for $C_{20}H_{28}O_5$:348.1929; found for $C_{20}H_{28}O_5$: 348.1937.

Mono(3,5-di-tert-butyl-(4-hydroxymethyl)benzyl itaconate (1.15 g, 3.3 mmol) was treated with a 1M solution of Bu_4NOH in methanol (3.3ml, 3.3mmol Bu_4NOH) to yield the desired Bu_4Ncarboxylate salt, which was isolated by removing methanol under vacuum. BIIR (11 g) and Bu_4NBr (0.53 g, 1.65 mmol) were dissolved in toluene (100 g) and heated to 85°C for 180 min. Bu_4Ncarboxylate salt (1.96 g, 3.3 mmol) was added before heating the reaction mixture to 85°C for 60 min. The esterification product was isolated by precipitation from excess acetone, purified by dissolution/precipitation using hexanes/acetone, and dried under vacuum, yielding IIR-g-BHT itaconate. ^{1}H-NMR ($CDCl_3$) : δ 6.24 (s, C**H_2**=C(CH_2)-COO-, 1H), δ 5.62 (s, C**H_2**=C(CH_2)-COO-, 1H), δ 3.36 (s, CH_2=C(C**H_2**)-COO-, 2H), δ 5.32 (s, Ar-C**H_2**-O-CO-, 2H), δ 4.54 (E-ester, =CH-**CH_2**-OCO-, 2H, s), δ 4.60 (Z-ester, =CH-**CH_2**-OCO-, 2H, s).

Synthesis of IIR-g-perfluorooctyl itaconate: 1H,1H,2H,2H-Perfluoro-1-octanol (4.58mmol,1.66g), itaconic anhydride(5.03mmol,0.56g), were dissolved in toluene (10g) and heated to 80°C for 4hr. Residual starting materials and solvent were removed by Kugelrohr distillation (T= 80°C, P=0.6mmHg).

The resulting acid-ester (1.57 g, 3.3mmol) was treated with a 1M solution of Bu_4NOH in methanol (3.3ml, 3.3mmol Bu_4NOH) to yield the desired Bu_4Ncarboxylate salt, which was isolated by removing methanol under vacuum. ^{1}H-NMR ($CDCl_3$) : δ 6.24 (s, C**H$_2$**=C(CH_2)-COO-, 1H), δ 5.62 (s, C**H$_2$**=C(CH_2)-COO-, 1H), δ 3.36 (s, CH_2=C(C**H$_2$**)-COO-, 2H), δ 3.99-4.01 (t,=C(CH_2)-COO-C**H$_2$**-CH_2-, 2H), δ 2.36-2.39 (m,=C(CH_2)-COO-CH_2-C**H$_2$**-CF_2-, 2H). HR MS calculated for $C_{13}H_9O_4F_{13}$:476.0293; found for $C_{13}H_9O_4F_{13}$: 476.0299.

BIIR (11g) and Bu_4NBr (0.53 g, 1.65mmol) were dissolved in toluene (100g) and heated to 85°C for 180 min. Bu_4Ncarboxylate salt (2.366g, 3.3mmol) was added before heating the reaction mixture to 85°C for 60 min. The esterification product was isolated by precipitation from excess acetone, purified by dissolution/precipitation using hexanes/acetone, and dried under vacuum, yielding IIR-g-perfluorooctyl itaconate. ^{1}H-NMR ($CDCl_3$) : δ 6.24 (s, C**H$_2$**=C(CH_2)-COO-, 1H), δ 5.62 (s, C**H$_2$**=C(CH_2)-COO-, 1H), δ 3.36 (s, CH_2=C(C**H$_2$**)-COO-, 2H), δ 4.10-4.13 (t, CH_2=C(CH_2)-COO-C**H$_2$**-CH_2-, 2H), δ 4.54 (E-ester, =CH-**CH$_2$**-OCO-, 2H, s), δ 4.60 (Z-ester, =CH-**CH$_2$**-OCO-, 2H, s), δ 3.81-3.83 (t,=C(CH_2)-COO-C**H$_2$**-CH_2-), δ 2.37-2.40 (m,=C(CH_2)-COO-CH_2-C**H$_2$**-CF_2-, 2H).

Synthesis of IIR-*g*-perfluorooctyl succinate

1H,1H,2H,2H-Perfluoro-1-octanol (4.58 mmol, 1.66 g), succinic anhydride (5.03mmol,0.56g), were dissolved in toluene (10g) and heated to 80°C for 4hr. Residual starting materials and solvent were removed by Kugelrohr distillation (T= 80°C, P=0.6mmHg). The resulting acid-ester (1.57 g, 3.3mmol) was treated with a 1M solution of Bu_4NOH in methanol (3.3ml, 3.3mmol Bu_4NOH) to yield the desired Bu_4Ncarboxylate salt, which was isolated by removing methanol under vacuum. ^{1}H-NMR ($CDCl_3$): δ 2.67-2.69 (m, HOOC-CH_2-C**H$_2$**-COO-, 2H), δ 2.65-2.63 (m, HOOC-C**H$_2$**-CH_2-COO-, 2H), δ 4.38-4.40 (t, HOOC-CH_2-CH_2-COO-C**H$_2$**-CH_2-, 2H), δ 2.45-2.47 (m,HOOC-CH_2-CH_2-COO-CH_2-C**H$_2$**-CF_2-, 2H). HR MS calculated for $C_{12}H_9O_4F_{13}$:464.0293; found for $C_{12}H_9O_4F_{13}$: 464.0287.

BIIR (11g) and Bu_4NBr (0.53 g, 1.65 mmol) were dissolved in toluene (100 g) and heated to 85°C for 180 min. Bu_4Ncarboxylate salt (2.366 g, 3.3 mmol) was added before heating the reaction mixture to 85°C for 60 min. The esterification product was isolated by precipitation from excess acetone, purified by dissolution/precipitation using hexanes/acetone, and dried under vacuum, yielding IIR-g-perfluorooctyl itaconate. ^{1}H-NMR ($CDCl_3$) : ^{1}H-NMR ($CDCl_3$): δ 3.93 - 3.91 (t, -CH_2-CH_2-COO-C**H_2**-, 2H), δ 3.35 (s, OOC -C**H_2**-C**H_2**-COO-, 4H), δ 2.44 -2.47 (m,-CH_2-COO-CH_2-C**H_2**-CF_2-, 2H), δ 4.48 (E-ester, =C-**CH_2**-OCO-, 2H, s), δ 4.50 (Z-ester, =C-**CH_2**-OCO-, 2H, s)

Synthesis of Zn-di-dodecyl itaconate

Dodecylitaconic acid (3.5 g, 11.7 mmol) and zinc oxide (0.47 g, 5.87 mmol) were heated to 85°C in a round bottom flask for 120 min. The hot mixture was then dissolved in 25 ml of THF followed by the addition of $MgSO_4$ and the solution for stirred for 120 min. After filtering off $MgSO_4$, THF was removed using Kugulrohr distillation (50°C, 0.6 mmHg). HR-MS calculated for $C_{17}H_{29}O_4$: 297.2060; found for $C_{17}H_{29}O_4$: 297.2054. m.p: 52-55°C

Synthesis of Na-dodecylitaconate

Dodecylitaconic acid (3.5 g, 11.7 mmol) and sodium hydroxide (0.47 g, 11.7 mmol) were mixed with 10 ml of methanol and reacted at 25°C for 24hrs. Methanol was removed using Kugulrohr distillation (80°C, 0.6mmHg) and sodium dodecylitaconate was isolated by recrystallization from diethylether solution. HR-MS calculated for $C_{17}H_{29}O_4$: 297.2066; found for $C_{17}H_{29}O_4$: 297.2063. m.p: 45-47°C

Instrumentation and Analysis: ^{1}H-NMR spectra were acquired in $CDCl_3$ on a Bruker Avance-600 spectrometer. Mass spectra were obtained on an Applied Biosystems QStar XL QqTOF mass

spectrometer. Dynamic shear modulus measurements were recorded using an Alpha Technologies, Advanced Polymer Analyzer 2000. Pressed samples of elastomer were coated with the required amount of a stock solution of DCP in acetone, and allowed to dry prior to passing three times through a 2-roll mill. This mixed compound was cured in the rheometer cavity at 3° oscillation arc and a frequency of 1 Hz.

Contact angle measurements:

Contact angle measured using sessile drop method. A 15% solution of rubber samples in hexanes were cast on thin strips of aluminium of dimension 2cm X 6cm and dried for 24 h to form a smooth surface. Images of droplets of the liquids (5µL) on the rubber surface exposed to air were analysed using the droplet snake method on a computer equipped with a camera. Three replicate measurements were made for each sample with mean values reported.

Extrudate Analysis:

1g rubber samples were extruded out of a Tinius Olsen apparatus at 140°C with a 10.0 kg load. Te extrudates were examined with a Olympus system microscope equipped with Polaroid digital microscope camera for capturing images of the specimen.

Tensile testing

40.0 g of dried rubber was coated with the required amount of a solution of DCP in acetone and allowed to dry before being passed through a two roll mill ten times. The rubber sample was compression molded at 160°C and 20 MPa for 25 min to a thickness of 2.00 ±0.05 mm. Specimens for tensile testing were cut from the cured sheet using a dog bone cutter described in ASTM D4482.

Tensile testing was done using an INSTRON Series 3360 universal testing instrument, operating at a crosshead speed of 500 mm/min at 23 ± 1 °C. Five replicate measurements were made for each sample with mean values reported.

Compression set measurements:

2g of the rubber samples were placed inside a cylindrical mold with a diameter of 14.0 mm and a height of 12.5 mm. The samples were cured at 160 °C for 25 min. The final cylinders had a diameter of 14 ± 0.1 mm and a height of 12.5 ± 0.2 mm. Compression set measurements were carried out using a pneumatic press. The samples were compressed with 3.5 MPa to a 45% strain using a stainless steel spacer for 22 h. The samples were removed after 22 h and allowed to rest for 30 min before the final height of the cylinders was measured. The compression set values were calculated according to ASTM D395 – 03.

5.3. Results and Discussion

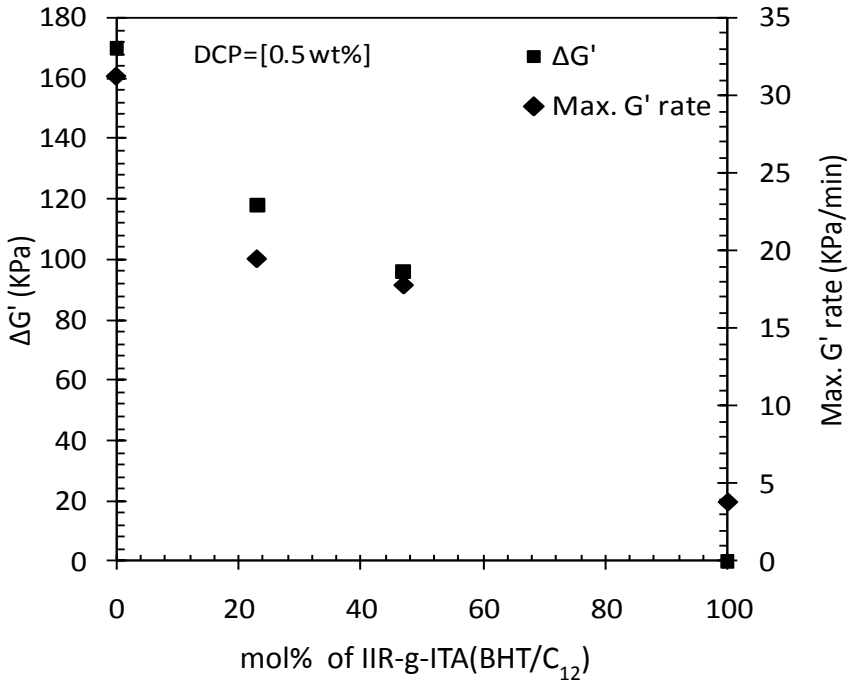
5.3.1. IIR-g-dodecylitaconate with bound anti-oxidant

Polymers are protected against oxidation by the usage of anti-oxidants in the formulations. Some of the most commonly used are amine based compounds and hindered phenols. Amine derivatives are not the most popular anti-oxidant because of its tendency to stain the polymer once participating in the radical quenching activity. Hindered phenols do not suffer from such concerns, as a result are more widely used in stabilizing elastomers.[2] Anti-oxidants operate by readily donating a labile hydrogen atom to any source of free radical, hence quenching radical activity and protecting the polymer chains from radical attack. One of the most commonly used hindered phenol for this purpose is butylated hydroxy toluene or 2,6-di-*tert*-butyl-4-methylphenol (BHT).

The ability of BHT to donate hydrogen atom to a radical species is well established.[3] Hogg et al., reacted several phenolic derivatives with a 2,2-diphenyl-1-picrylhyclrazy free radical and observed the disappearance of the free radical using infra-red measurements. They concluded that the rate of consumption of 2,2-diphenyl-1-picrylhyclrazy was first order with respect to BHT. Similar examination of BHT was also reported by Bondet et al.[4] In both cases, the energy of activation for these reactions were reported to be 25 KJ/mol, suggesting that the reaction is thermodynamically feasible. The stability of the BHT radical formed has not been discussed in either of the reports as they did not carry out characterization of the reaction products.

Commercially available polymers contain antioxidants in significant quantities, as result they contribute towards leachables and extractables. Sensitive applications which demand low concentrations of leachables and extractables cannot accommodate significant quantities of AO. Hence the idea of polymer bound anti-oxidant has received great attention. The most commonly reported pathway of delivering AO as polymer bound entity is through radical mediated grafting of monomers containing an AO functional group. Kim et al grafted PE with a maleimide based compound containing BHT group in it.[5] But they reported a decrease in graft yield with the increase in monomer concentration at fixed peroxide loading. Similarly, acrylated and methacrylated BHT was grafted onto HDPE and LDPE in the presence of a peroxide initiator.[6] The effect of concentration of monomers on the graft yield was not reported. Similar methods were also reported elsewhere.[7,8] However, the AO present in the monomer will scavenge the radical generated by the peroxides in the very radical mediated process through which it is being bound to the polymer. This not only reduces the graft yields but also reduces the concentration of the potent polymer bound AO.

In the previous chapters, the instability of butyl rubber based macromonomers was discussed in detail. IIR-g-itaconate derivatives provide a novel synthetic route for stabilizing the macromonomer through bound AO. Itaconic anhydride was treated with hydroxyl terminated BHT to yield butylatedhydroxy toluyl itaconic acid. The IIR-g-ITA was equipped with varying degrees of BHT through mixed alkylation of BIIR with mono-dodecyl itaconic acid and butylatedhydroxy toluyl itaconic acid as nucleophiles in appropriate ratios. The carboxylate anions had similar reactivity with respect to nucleophilic substitution of BIIR. The effect of varying concentration of bound BHT on the peroxide cure yield and stability is illustrated in Figure 5.1.



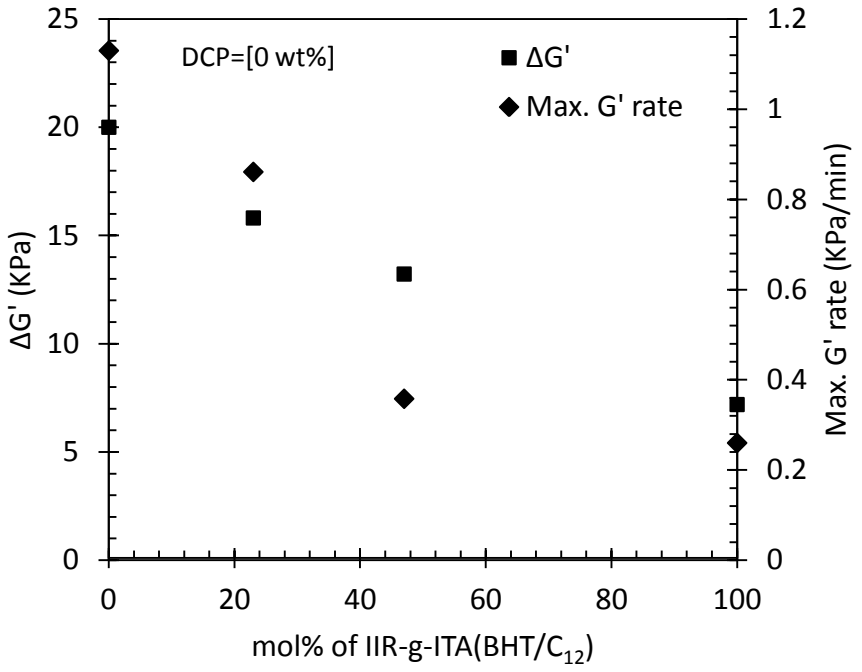


Figure 5.1: Dynamics of cross-linking of IIR-g-ITA (BHT/C_{12}) derivatives

The upper limit posed by BIIR only allows a maximum of 0.15mmol/g of functional groups. The peroxide cure rate and yield of IIR-g-dodceyl itaconate was demonstrated in the previous chapter. The introduction of bound BHT in the place of dodecyl groups have an expected effect on the rate of peroxide cure and yield (Figure.). Since the oxygen centred radicals resulting from the peroxide initiator decomposition prefers to abstract hydrogen abstraction, some of these radicals can be expected to be consumed by BHT which is an excellent hydrogen atom donor. This results in the reduction of the amount of peroxide radicals available for the cure.

The cure formulation for IIR-g-ITA (BHT/C_{12}) contained 0.5 wt% DCP, which translates to 36µmol/g of radicals. The IIR-g-ITA with 100% BHT has peroxide radical to BHT ratio of 1:4 resulting in the complete suppression of the cure. However, the hydrogen atom donation of the BHT cannot be considered as the dominant reaction taking place as IIR-g-ITA (BHT/C_{12}) with 47% and 23% BHT (1:2 and 1:1 peroxide to

BHT) resulted in curing of the polymer. This suggests that the interference of BHT in the cure is a competing reaction with the cross-linking reaction. The BHT in the polymer still consumes radicals which is reflected in the reduction of the G' rate and the yield of the peroxide cure.

In the absence of peroxides, the reactive macromonomers were still shown to be active and cross-link over a period of time at high temperatures. However, the mechanism through which the cross-linking occurs is unknown. Similar to the peroxide cures, the presence of BHT in the polymer reduces the cure yields. The design of the IIR-*g*-ITA (BHT/C_{12}) has to take into account that the polymer needs to be cross-linked in the end and the amount BHT in the polymer needs to be appropriate to stabilize the polymer as well as allowing it to peroxide cure when required.

5.3.2. Grafting of BIIR with Tridecafluorooctyl Itaconic Acid (IIR-g-ITA(C_8F_{13})) and Tridecafluorooctylsuccinic Acid (IIR-g-SUC(C_8F_{13}))

Fluorocarbon-based polymers are well known for being low surface energy materials. Hence, these polymers are used as processing aids in the extrusion of polymers.[9] Flow instabilities such as shark skin and melt fracture during extrusion of polymers are overcome by using the fluorocarbon-based polymers in low concentrations (1000 ppm). These processing aids are believed to be immiscible with the host polymer and migrate to the surface of the polymer thereby reducing the friction between the die-wall and the polymer resulting in stable flow of the polymer.

Additionally these types of materials are commonly used as coatings for BIIR- and BIMS-based stoppers used for pharmaceutical applications.[10] Consequently we felt it would be of interest to introduce a fluorocarbon phase into butyl rubber through the use of itaconates. The first material examined was IIR modified with an itaconate half-ester of a fluorinated alcohol (tridecafluorooctanol). As shown in Figure

5.2, this material produced a very similar cure profile to that of IIR-g-ITA(C_{12}) indicating that the fluorous phase has no noticeable effects on peroxide cure dynamics.

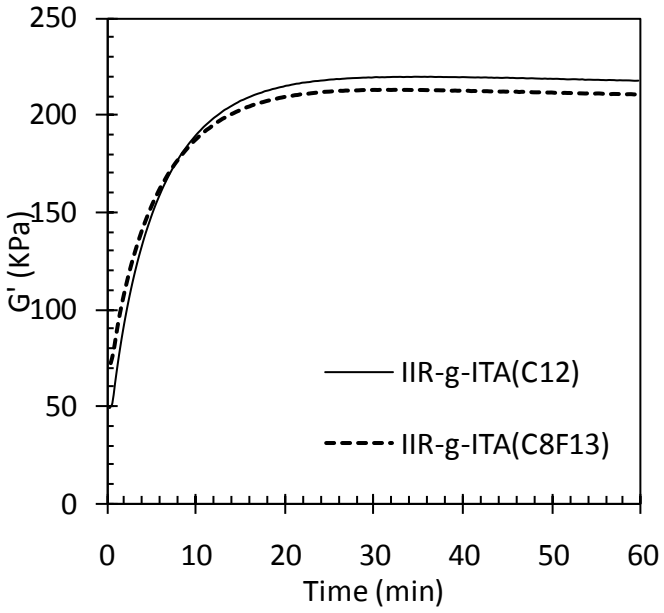


Figure 5.2: Dynamics of peroxide-initiated crosslinking of IIR-g-ITA(C_8F_{13}) at 160°C (0.5 wt% DCP).

For surface energy measurements, a series of materials were made in which BIIR was alkylated with differing mole ratios of a hydrocarbon ester (acetate) to fluorocarbon ester (mono(tridecafluorooctyl) succinate) IIR-g-ITA(C_8F_{13} / acetate). Succinate was chosen as a thermally stable linker for the fluorocarbon ester. A family of low molecular weight hydrocarbons were used as liquids for surface energy measurements by sessile drop technique. The critical surface energy measurements shown in Figure 5.3 indicate, as expected, that the surface energy decreases as the mole fraction of the fluorocarbon ester increases. At this stage we do not know if the fluorous phase is distributed uniformly throughout these materials, or whether it has phase-separated and migrated predominantly to the surface of these materials.

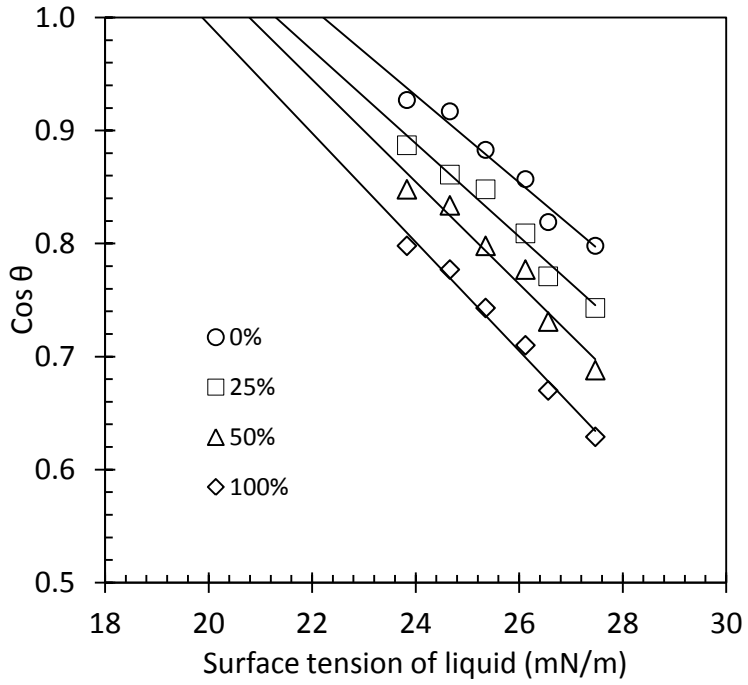


Figure 5.3: Surface energy of IIR grafted with increasing ratios of tridecafluorooctyl succinate (C_8F_{13}) to acetate (0 = 100% acetate).

The IIR-g-SUC(C_8F_{13}) was extruded through a die using a 10Kg load at 140°C. The extrudate from the low shear extrusion was collected and examined using a microscope equipped with a camera and the images of the extrudate, captured at a 10X magnification is shown in the Figure 5.4. The reduction in surface energy clearly affects the flow characteristics of the extrudate. Although, the extrudate was obtained using a low shear rate process, the evidence of the ability of the fluorocarbon to stabilise flow of IIR-g-SUC (C_8F_{13}) is very substantial.

Figure 5.4: Images of extrudate of IIR (left) and IIR-g-SUC(C_8F_{13}) (right) at a 10x magnification

5.3.3. Co-agent cures of IIR-g-ITA(C12) with Zn(dodecyl itaconate)$_2$

Zinc diacrylate and zinc dimethacrylate are co-agents which have been used in peroxide cures of elastomers to improve elastomer performance through improved mechanical, thermal and chemical resistance properties. For example, peroxide-cured HNBR/Zn dimethacrylate blends have been shown to have improved low temperature performance and heat resistance. Peroxide cured EPDM/Zn dimethacrylate have been shown to have superior flex fatigue resistance and tear strength. Improved adhesion to metal has also been reported for peroxide cured EPDM/Zn diacrylate.[11] These co-agents are however high melting solids which do not disperse well in an elastomer matrix, consequently it would be of interest to evaluate Zn(dodecyl itaconate)$_2$ as an alternative co-agent for use with IIR-g-ITA(C_{12}). Zn(dodecyl itaconate)$_2$ was prepared by reaction of monododecyl itaconate with ZnO to give a low melting solid (mp 52-55°C). Sodium dodecyl itaconate was similarly prepared by reaction with NaOH.

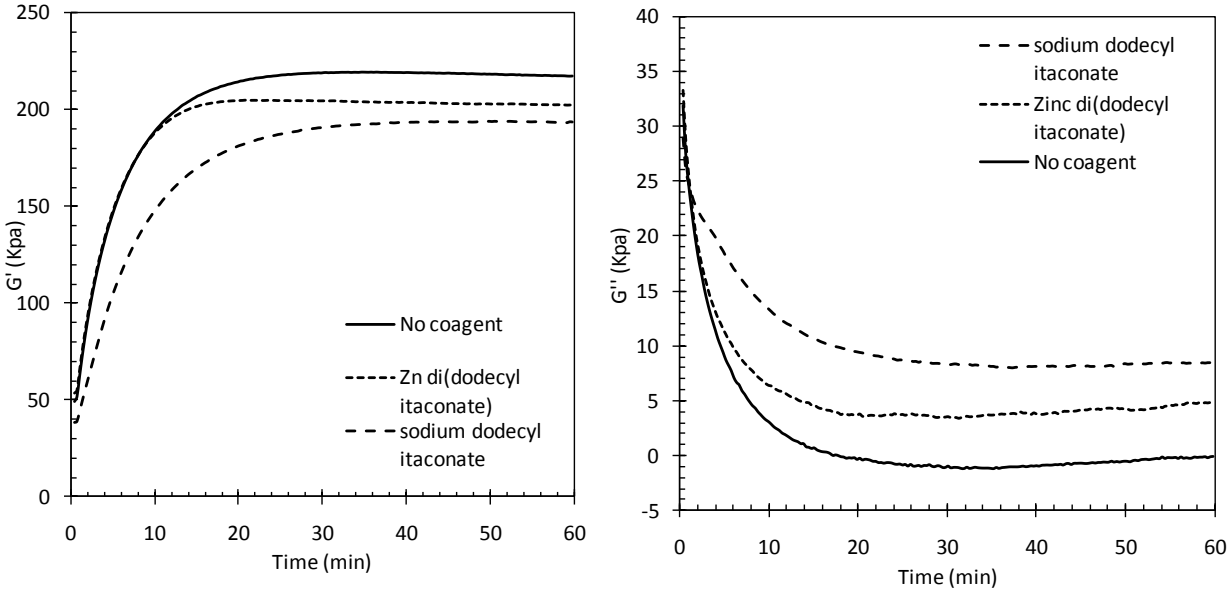


Figure 5.5: Dynamics of peroxide-initiated crosslinking of IIR-g-ITA(C_{12}) in the presence and absence of co-agents; 160°C and 0.5 wt% DCP. Mole ratio of covalent itaconate to ionic itaconate = 1:1 (Zn di(dodecyl itaconate) : 0.075mmol/g of rubber; Na dodecyl itaconate: 0.15mmol/g of rubber)

The peroxide cure dynamics of IIR-g-ITA(C_{12})/coagents is illustrated in the Figure 5.5. As indicated in the Figure, the concentration of coagents were normalized to contain itaconate equivalent to IIR-g-ITA(C_{12}). The peroxide loading however remained at 0.5wt%. Consequently, the cure yield for IIR-g-ITA(C_{12}) without coagent was higher as the amount of itaconate to be consumed per radical was the lowest compared to the IIR-g-ITA(C_{12})/Zn di(dodecyl itaconate) and sodium dodecyl itaconate formulations. The IIR-g-ITA(C_{12})/Zn di(dodecyl itaconate) and sodium dodecyl itaconate both had twice as much itaconate as IIR-g-ITA(C_{12}) alone. However, in the case of Zn di(dodecyl itaconate), since it is a bi-functional coagent, every second addition of the same coagent molecule to the oligomerization of the polymer bound itaconate results in cross-linking of the oligomerizing chains. In the case of sodium dodecyl itaconate, addition to the oligomerizing of polymer bound itaconate dilutes the cross-linking density.

In both cases, the covalently bound coagents are expected to participate in ionic aggregation within the polymer. The high loss modulus exhibited by the IIR-g-ITA(C_{12}) peroxide cured with ionic coagents

suggests that there is dissipation of energy, presumably, through the labile ionic networks. Hence, the peroxide cured IIR-g-ITA(C_{12})/ Zn di(dodecylitaconate) and IIR-g-ITA(C_{12})/Na dodecylitaconate contains both covalent cross-linked networks as well as ionic networks.

Table 5.1: Effects of co-agents on tensile strength, elongation at break and compression set for peroxide cross-linked IIR-g-ITA(C_{12})

IIR-g-ITA	Tensile strength (Mpa)	Elongation at break (%)	Compression set (%)
No coagent	0.7	401	2.0
Sodium dodecylitaconate	0.9	524	4.6
Zinc di(dodecylitaconate)	1.6	615	10.1

The effect of the hybrid networks containing both ionic and covalent cross-links is reflected on the mechanical properties of the polymer (Table 5.1). The tensile strength and elongation at break were improved by the addition of the ionic coagents which is reflective of the ionic network contribution. Similarly the effect of the ionic networks were also seen in the compression set behaviour of the polymers as the incorporation of the coagents into the polymer network diminished the ability of the polymer to retain its dimensions after compressive deformation. This behaviour, similar to the loss modulus, can be attributed to the labile nature of the ionic networks.

5.4.Conclusion:

Several derivatives based on IIR-g-ITA were prepared by alkylating BIIR using various itaconic anhydride half-ester as the nucleophile. IIR-g-ITA(BHT/C_{12}) at low concentrations was shown to stabilise the polymer with respect to radical activity along with retaining the ability to cross-link in the presence of low concentrations of peroxide. IIR was grafted with fluorocarbon chains which reduced the surface energy of the polymer thereby providing smooth flow characteristics at low shear rate. Hybrid networks containing both covalent and ionic networks were introduced into IIR-g-ITA(C_{12}) by peroxide curing it with ionic coagents in the form of zinc and sodium salts of mono dodecylitaconic acid The ionic network improved the tensile properties while lowering the compression set resistance.

5.5. References:

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Chapter 6 : Conclusions and Recommendations

6.1.Conclusions

The mechanisms through which maleimides enhance the efficacy of peroxide cure formulations when applied to saturated and unsaturated polymers have been estsablished. N-arylmaleimide coagents engage saturated polymers such as LLDPE through C-H bond addition, the efficiency of which may be affected by the polymer's reactivity toward hydrogen atom donation. In contrast, unsaturated polymers can be cross-linked by an alternating copolymerization that is affected by the unsaturation content of the material as well as the degree of substitution about its C=C functionality.

Commercial grades of isobutylene-rich elastomers do not cure under the action of peroxides. However, the high reactivity of allylic bromide functionality in the BIIR can be exploited in making IIR derivatives that are reactive towards peroxide curing. Poly(isobutylene-co-isoprene) elastomers containing 2-6 mole% IP are unreactive to peroxide-only cure formulations, but cross-link with limited efficiency when combined with a bis-maleimide coagent. With knowledge of the underlying mechanisms through which bis-maleimide coagents enhance the efficiency of peroxide cure of polymers, isobutylene rich elastomers bearing two distinct types of functionalities were prepared. Co-curing elastomers bearing pendant polyether functionality provide higher cross-linking yields, owing to their reactivity in C-H bond addition to N-aryl maleimides. Similarly, sterically unencumbered, electron-rich olefin functionality can provide exceptional cross-linking rates and yields due to their ability to engage maleimides in alternating copolymerization.

An alternative approach to making IIR peroxide cure is to prepare macro-monomers of IIR bearing oligomerizable C=C functionality. These materials undergo simultaneous cross-linking and degradation when activated by radical initiators, with the competitive balance dictated by the reactivity of the

oligomerizable group. Highly reactive maleimide, styrenic and acrylate functionality provides good peroxide cure activity at the expense of storage and compounding stability, while less reactive maleate esters and unactivated vinyl groups provide good stability at the expense of peroxide cure extent. Surprisingly, nitroxyls can mitigate free radical cure activity, but do not prevent auto-initiation.

IIR macromonomers containing itaconate and methacrylate pendant groups provide the best balance between cure reactivity and stability. However, only itaconate esters provide a platform for adding another functionality that is capable of modifying physical and/or chemical properties of the elastomer. Several derivatives based on IIR-g-ITA were prepared by alkylating BIIR using various itaconic anhydride half-ester as the nucleophile. IIR-g-ITA(BHT/C_{12}) at low concentrations stabilises the polymer with respect to radical activity along with retaining the ability to cross-link in the presence of low concentrations of peroxide. IIR was grafted with fluorocarbon chains which reduced the surface energy of the polymer thereby providing smooth flow characteristics at low shear rate. Hybrid networks containing both covalent and ionic networks were introduced into IIR-g-ITA(C_{12}) by peroxide curing it with ionic coagents in the form of zinc and sodium salts of mono dodecylitaconic acid. The ionic network improved the tensile properties while lowering the compression set resistance.

6.2.Recommendations

a. The rheological measurements done in this research to monitor cross-link yields were carried out at high strains (3° arc). Such high strains could be disruptive to the cross-linked networks and as such lower strains could be used in the future measurements.

b. The reason behind the instability of some of the macromonomers prepared in this investigation is unclear. Although some evidence indicate that the functionalities might be unstable with respect to nucleophilic addition, further investigation is required to establish the cause.

c. In addition to the functional macromonomer derivatives of IIR reported in this investigation, several other functionalities need to be explored. Amine nucleophiles that can be used to ring open itaconic anhydride may open the doors for several new functional macromonomers. For example, IIR containing amino silane functional groups has the potential to enhance silica dispersion within the polymer.

d. Very little has been reported on the peroxide cures of halobutyl rubbers. The successful peroxide curing of the halobutyl rubbers offers an attractive pathway for creating IIR thermosets.

6.3. Scholarly Contributions and Technology Development

- Karthik V. S. Shanmugam, J.Scott Parent, Ralph A. Whitney, "C-H Bond Addition and Copolymerization Reactions of N-Arylmalemides: Fundamentals of Coagent-assisted Polymer Cross-linking," European Polymer Journal, Volume 48, Issue 4, April 2012, Pages 841-849
- Karthik V. S. Shanmugam, J. Scott Parent, Ralph A. Whitney, "Design, synthesis and characterization of bismaleimide co-curing butyl rubber derivatives ," Ind. Eng. Chem. Res., 2012.
- J. Scott Parent, Ralph A. Whitney, Karthik V. S. Shanmugam –" Free-radical Stable Polymers that are Curable in the Presence of Co-agent" Provisional United States Patent Application 61/345,396 filed May 17, 2010.
- J. Scott Parent, Ralph A. Whitney, Karthik V. S. Shanmugam –" Free-radical Curable Functional Macromonomers Prepared from Anhydride" Provisional United States Patent Application 61/345,400 filed May 17, 2010.