Synthesis and Characterization of Ionically Crosslinked Elastomers

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ABSTRACT
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Technical Report: Synthesis and Characterization of Ionically Crosslinked Elastomers

Kevin Cavicchi, Guodong Deng, Jehoon Lee

Department of Polymer Engineering, The University of Akron, Akron, OH 44325-0301

Introduction: The driving hypothesis of this work was that organic ion pairs represent an underutilized non-covalent dynamic bond that is useful for the development of responsive polymers. To test this hypothesis ionically crosslinked elastomers were chosen as a model system to study the thermomechanical response of ion-pair crosslinks. Previous work had synthesized ionically crosslinked poly(n-butylacrylate) using a three step route of the synthesis of a cationic ionomer, ion-exchange of the ionomer with a anionic monomer, and crosslinking by copolymerization with a hydrophobic monomer. While these materials displayed signatures of thermomechanically dependent dynamic bonding, the synthesis inherently produced heterogeneous crosslinked networks and was difficult to systematically modify (e.g. the choice of cation and crosslink density) without redoing the entire synthesis. Two alternate methods of model ionically crosslinked network synthesis were investigated:

1. Polymerization using a reversible addition fragmentation chain transfer (RAFT) agent containing an ion-paired crosslinking groups (i.e. RAFT crosslinking agent).
2. Polymerization using an ion-pair crosslinking agent.

Summary of Accomplishments: The following summarizes the accomplishments of this work, which are described in more detail in the following two sections.

1. Developed synthesis of RAFT agents capable of acting as crosslinkers (i.e. RAFT agent crosslinker) in free radical polymerization. RAFT agents with two styrenic functionalities were synthesized that are attached either covalently or ionically to the central trithiocarbonate group. From the study of the covalent RAFT agent crosslinkers it was found that the crosslink density could be controlled through the concentration of RAFT agent in the polymerization. In polymerizations with both the covalent and ionic crosslinkers, covalently crosslinked networks were obtained. In the case of the ionic crosslinker, this was thought to be due to interchain transfer reactions at high conversion that introduce chain branching (i.e. dangling chains), with a similar mechanism thought to occur with the covalent RAFT agent crosslinker. This results in materials with very low moduli and higher damping above room temperature. Therefore, these RAFT agents should have utility in the synthesis of super-soft and/or higher damping elastomers.

2. An ionic, divinyl crosslinking agent (i.e. vinyl benzyl tri-n-octylammonium styrene sulfonate) was synthesized that could crosslink poly(n-butylacrylate) by solution and melt polymerization. These systems show characteristics of ion-pair crosslinks, that are insoluble in solution, but can dissolved in acidic media or compression molded at higher temperature. This one-pot reaction polymerization procedure is a significant improvement over the previous three step synthetic method and will be useful for the study of ionically crosslinked elastomers.
**RAFT Crosslinking Agent:** The synthesis of the RAFT crosslinking agent is shown in Figure 1a. The quaternary ammonium monomer was prepared by quaternization of vinyl benzyl chloride, while a common dicarboxylic RAFT agent was neutralized with potassium. The ideal structure of the crosslinked network prepared with this agent is shown in Figure 1b. Here network junctions consist of one strand covalently bonded to the trithiocarbonate group of the RAFT agent and two ionically linked strands. This synthesis was designed to reduce the number of polymerization steps compared to the previous three step route; largely eliminate chain ends due to chain initiation; more homogeneously distribute the ion-pair crosslinks; and allow control over the crosslink density. Here the crosslink density is controlled by the concentration of RAFT agent crosslinker in the polymerization where each mole of RAFT agent will produce one mole of crosslink junctions.

Initial polymerizations of *n*-butyl acrylate (BA) were conducted in 50% chlorobenzene solutions, however these did not form good elastomer samples. This RAFT crosslinking agent was also found to be insoluble in BA monomer. Therefore, a two-step polymerization procedure was undertaken to prepare ionically crosslinked networks. In the first step, *n*-butyl acrylate was polymerized with the RAFT crosslinking agent in methanol to low conversion to introduce BA units, but limit the crosslinking reactions of the vinylbenzyl tri-*n*-butylammonium units. The oligomers were prepared by a 1h polymerization targeting different crosslink densities. Each oligomer was then dissolved in *n*-BA at a concentration to target the same crosslink density as the oligomer polymerization and poly(*n*-butylacrylate) (PBA) networks were prepared in the melt.

Samples were prepared with target crosslink densities \(v_{\text{target}}\) from 13.4 to 268.2 \(\text{mol/m}^3\). Gel fractions of ca. 80% and monomer conversions of > 90% were observed for these samples. These samples all swelled rather than dissolved in tetrahydrofuran and acetone, two good solvents for these polymers, consistent with a crosslinked network. In contrast to the previous three-step polymerization systems, these samples could not be dissolved in THF once hydrochloric acid was added to dissociate the ion-pairs. In addition, it was difficult to compression mold these samples into flat discs for rheology characterization. Therefore, they were polymerized as large discs in a septum capped jar, and rheology samples were cut out using a die punch. The samples were characterized by oscillatory shear in the linear viscoelastic limit. Figure 2 shows the master curves of the storage \((G')\) and loss \((G'')\) moduli and the tan \(\delta\) \((G''/G')\). Here \(G' > G''\) over the entire frequency range and \(G'\) is tending to plateau at low
frequency while $G''$ continues to decrease. This is consistent with a crosslinked network. However, the plateau modulus at low frequency was much lower than expected ($G''_p = \nu/RT$), giving $\nu = 3.8$ mol/m$^3$ and 4.2 mol/m$^3$ for the 13.4 to 26.8 mol/m$^3$ targets.

**Figure 2.** Master curves for target crosslink densities of (a) $\nu_{\text{target}} = 26.8$ mol/m$^3$ (b) $\nu_{\text{target}} = 13.4$ mol/m$^3$.

One explanation for these results is that covalent crosslinking takes place during the polymerization. A likely mechanism for this is the intermolecular chain transfer to either the PBA backbone or benzyl methylene group in the benzyl tri-$n$-butylammonium (B-TBA) cation. For example, intermolecular chain transfer has previously been observed in the RAFT polymerization of PBA stars at high conversion.$^1$ A schematic of this for chain transfer to the PBA backbone is shown in Figure 3. The result of this chain transfer either to the PBA or

**Figure 3.** Chain transfer cycle replacing one ionically connected crosslink strand with a covalently connected strand.
B-TBA is the replacement of ion-pair in a tri-functional crosslink with a covalent bond and the formation of a graft connected to the main chain by an ion-pair. Therefore, multiple chain transfer reactions would result in the formation of a covalent network. From the plateau moduli in Figure 2 this would require 28.64 and 15.81% chain transfer for the 13.41 to 26.82 mol/m³ target networks, respectively. Further supporting evidence of this mechanism is the large tan δ observed at low frequency. This would arise from the relaxation of the grafts, as has previously been observed in PBA comb polymer networks. This dynamic complexity complicates the study of the ion-pair crosslinks and their dynamics. Based on these results ion-pair crosslinks relax at a rate similar or faster to the grafts.

While ideal ionically crosslinked networks were not formed by this synthetic method the resulting materials are still highly interesting. In addition to showing damping far above the glass transition temperature of the polymer, the plateau moduli of these materials are also quite low for a melt polymerized polymer. Typically it is difficult to obtain plateau moduli below the entanglement plateau in a melt polymerization, while maintaining high gel fractions, due to the formation of trapped entanglements that act like permanent crosslinks. To investigate this phenomenon a covalent RAFT agent crosslinker was synthesized as shown in Figure 4a and use to synthesize covalently crosslinked PBA networks at target crosslink densities from \( v_{\text{target}} = 4.5 \) to 268.3 mol/m³. Figure 4b-c shows a plot of the swelling ratio in THF and gel fraction vs. target crosslink density, respectively. This swelling curve is consistent with the crosslink density scaling with the concentration of RAFT agent crosslinker in the polymerization. Master curves of \( G' \), \( G'' \) and tan δ for two different \( v_{\text{target}} \) are shown in Figure 5. Samples of higher \( v_{\text{target}} \) were extremely stiff and difficult to remove from the reaction jar without breaking. These curves are qualitatively identical to the ion-containing polymer networks in Figure 2. The large tan δ peak at lower frequency indicates that chain transfer to the PBA backbone likely also takes place in these systems producing graft side-chains. This indicates that the relaxation of any pair-crosslinks is likely fast, with the main contribution to the tan δ peak being from the graft chains. Finally, the ability to produce low moduli elastomers by melt polymerization is a consequence of the RAFT agent crosslinker and intermolecular chain transfer and should be widely applicable to different polymer chemistries.

In these covalent networks, the plateau

![Figure 4](image-url)

**Figure 4.** (a) synthesis of covalent RAFT agent crosslinker. (b) swelling ratio (Q) vs. \( v_{\text{target}} \). (c) Gel fraction vs. \( v_{\text{target}} \).
moduli scale with the target crosslink density. The crosslink density from the plateau moduli was used with the swelling data and the Flory-Rehner model to calculate the Flory-Huggins interaction parameter (χ) for PBA and THF to estimate the crosslink density of the higher νtarget samples. As shown in the plot in Figure 6, there is very good agreement between νcalculated and νtheory (calculated from νtarget taking the polymerization conversion into account). This indicates that this RAFT agent crosslinker provides excellent control over the crosslink density in these systems.

**Ion-Pair Crosslinking Agent:** To avoid the loss of ion-pair crosslinks due to intermolecular chain transfer a crosslinker (VBTOA-SS) was synthesized from vinylbenzyltri-n-octylammonium chloride (synthesis shown in Figure 7a) and sodium p-styrene sulfonate by metathesis ion exchange (Figure 7b). While previous attempts at crosslinking poly(n-butyl acrylate) using vinylbenzyltri-n-butylammonium p-styrene sulfonate were unsuccessful due to the insolvibility of the crosslinker in the acrylate, VBTOA-SS could be dissolved in a mixture of n-butyl acrylate and chlorobenzene and neat n-butyl acrylate. Two crosslinked samples were prepared: sample A was prepared with a 30% n-butyl acrylate solution in chlorobenzene with 6 mol% crosslinker (based on the n-butyl acrylate monomer) while sample B was prepared from melt
Both samples behaved in solution as crosslinked networks. They were swollen in solvent after polymerization to determine the gel fraction, which was measured as the ratio of the dry mass of the sample after swelling an extraction of the sol fraction to the target mass of the sample. Sample A was swollen in toluene and a gel fraction of 96% was measured. Sample B was swollen in chloroform and a gel fraction of 92% was measured. Both samples could be compression molded at 80°C to produce disc samples for rheology characterization (Figure 8). In addition, sample A could be dissolved in solution after the addition of either hydrochloric acid (HCl) or p-toluene sulfonic acid (pTSA) (Figure 9). Here the acid added in excess to the ion-pair concentration results in ion-exchange and the conversion of the ion-pair crosslinks into unlinked styrene sulfonic acid and either benzyl tri-n-octylammonium chloride (HCl) or benzyl tri-n-octylammonium p-toluene sulfonate (pTSA) groups.

Master curves for the rheological characterization of Sample A and Sample B are shown in Figure 10. In both cases, $G'$ is greater than $G''$ over the entire frequency range consistent with a more elastic behavior of the network. However, a plateau in $G'$ is not seen at lower frequency (higher temperature). It is speculated that the ion-pair crosslinks are dynamic and giving rise to the continuous relaxation of the network. More detailed rheological characterization including creep recovery and stress relaxation experiments are needed to fully characterize the thermomechanical properties of these materials.
References
