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14. ABSTRACT In this research poly(n-butyl acrylate) (PBA) elastomers were investigated as model systems to study the thermomechanical response of polymers crosslinked by organic ion pairs, where both the cation and anion are covalently bound to the polymer chain. Two main routes of polymer synthesis were investigated: (1) polymerization of n-butyl acrylate with a reversible addition fragmentation chain transfer (RAFT) agent containing polymerizable end-groups attached through an ion-pair (e.g. RAFT agent crosslinker) and (2) polymerization using an ion pair comonomer as a crosslinking agent. Both routes were found to produce crosslinked networks that were					
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Report Title

Final Report: STIR: Synthesis and Characterization of Ionically Crosslinked Elastomers

ABSTRACT

In this research poly(n-butyl acrylate) (PBA) elastomers were investigated as model systems to study the thermomechanical response of polymers crosslinked by organic ion pairs, where both the cation and anion are covalently bound to the polymer chain. Two main routes of polymer synthesis were investigated: (1) polymerization of n-butyl acrylate with a reversible addition fragmentation chain transfer (RAFT) agent containing polymerizable end-groups attached through an ion-pair (e.g. RAFT agent crosslinker) and (2) polymerization using an ion-pair comonomer as a crosslinking agent. Both routes were found to produce crosslinked networks that were insoluble in organic solvents that dissolve PBA. One challenge in these syntheses was the occurrence of mid-chain free radical transfer reactions that had a tendency to produce covalent crosslinks. These complicate the rheological characterization of these materials as two types of crosslinks are present in the network.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

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Number of Papers published in non peer-reviewed journals:

(c) Presentations

“Synthesis and Characterization of Ionically Crosslinked Networks” Session: Next Generation Smart Materials, 249th American Chemical Society Meeting, Denver, CO, March 2015

Number of Presentations: 1.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

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TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Jehonn Lee	0.90	
Guodong Deng	0.85	
FTE Equivalent:	1.75	
Total Number:	2	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Kevin Cavicchi	0.00	
FTE Equivalent:	0.00	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

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Names of Personnel receiving masters degrees

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Names of personnel receiving PHDs

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Total Number:

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
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Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Technology Transfer

See Attachment

List of Illustrations

Figure 1. RAFT agent crosslinkers (a) covalent, (b) ionic.

Figure 2. Master curve for crosslinked PBA (target crosslink density = $x \text{ mol/m}^3$)

Figure 3. Synthesis of (a) vinyl benzyl tri-*n*-octylammonium chloride and (b) vinyl benzyl tri-*n*-octylammonium styrene sulfonate (VBTOA-SS).

Figure 4. Master curves for PBA crosslinked with (a) 1 mol% and (b) 3 mol% VBTOA-SS. Measurements made from -30 to 170 °C with a $T_{\text{ref}} = 30 \text{ C}$.

Statement of the Problem Studied

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, where both the cation and anion are covalently bound to the polymer chain. Two polymerization routes for the preparation of ionically crosslinked networks were investigated:

1. Polymerization using a reversible addition fragmentation chain transfer (RAFT) agent containing polymerizable end-groups ionically bound to the RAFT agent
2. Polymerization using an ion-pair comonomer as a crosslinking agent

Summary of the Most Important Results

1. RAFT agents were synthesized that are capable of acting as both RAFT agent to control the free radical polymerization of a vinyl monomer and a crosslinking agent. RAFT agents with vinyl benzyl end-groups attached either covalently or ionically to the central trithiocarbonate group of the RAFT agent (Figure 1).

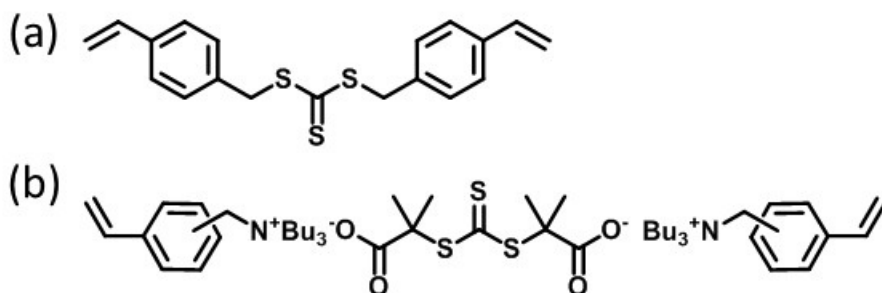


Figure 2. RAFT agent crosslinkers (a) covalent, (b) ionic.

Investigation of the covalent crosslinker in the polymerization of *n*-butyl acrylate showed that the crosslinking density could be controlled and was proportional to the concentration of RAFT agent in the polymerization. It was also found that at low crosslink densities plateau moduli below the entanglement modulus of poly(*n*-butylacrylate) (PBA) could be obtained (Figure 2). This indicates that entanglements are not trapped in these networks and that “supersoft” elastomers was synthesized (ca. 10 kPa modulus).¹ In addition a broad peak in $\tan \delta$ was observed above the glass transition of the polymer.

This is attributed to branching reaction during the polymerization due to intermolecular chain transfer of the radical to the backbone of the PBA.^{2,3} Therefore, it is not clear if the achievement of low plateau moduli and the prevention of trapped entanglements is due to the RAFT polymerization, the intermolecular chain transfer, or a combination of the two. This type of RAFT agent could be very useful for the polymerization of soft elastomers.

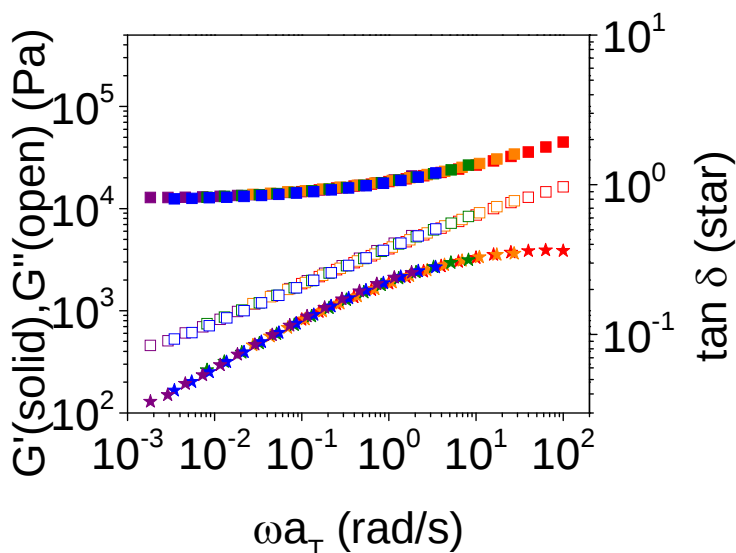


Figure 2. Master curve for crosslinked PBA (target crosslink density = 13.4 mol/m³)

Nearly identical master curves to those obtained using the ionic RAFT agent crosslinker. However, the plateau modulus and crosslink density were significantly lower than the target crosslink density based on the concentration of RAFT agent. This was attributed to the intermolecular chain transfer, which produced both ionic crosslinks and covalent crosslinks. Due to the similarity of the master curves of the covalent and ionically crosslinked networks it appears that the ammonium carboxylate ion-pairs exchange quickly above room temperature and do not act as effective crosslinks above room temperature.

2. An ion-pair comonomer vinylbenzyl tri-*n*-octylammonium styrene sulfonate (VBTOA-SS) was synthesized by the metathesis ion-exchange of vinyl benzyl tri-*n*-octylammonium chloride and sodium styrene sulfonate (Figure 3). VBTOA-SS was used for the crosslinking of PBA. Figure 4 shows the master curves for melt polymerized samples of PBA with 1 and 3 mol% VBTOA-SS. Evidence of ionic crosslinking is observed where the plateau modulus around a frequency of 1 rad/s increases with increasing VBTOA-SS concentration. Exchange of the ion-pairs is also evident due to the relaxation at lower frequencies. However, terminal relaxation of these samples is not observed. This is attributed to covalent crosslinking arising from interchain transfer reactions, which can be a persistent problem in PBA polymerizations.⁴ For future studies is a recommended that a monomer system less susceptible to chain transfer be investigation, such as *n*-alkyl methacrylates.

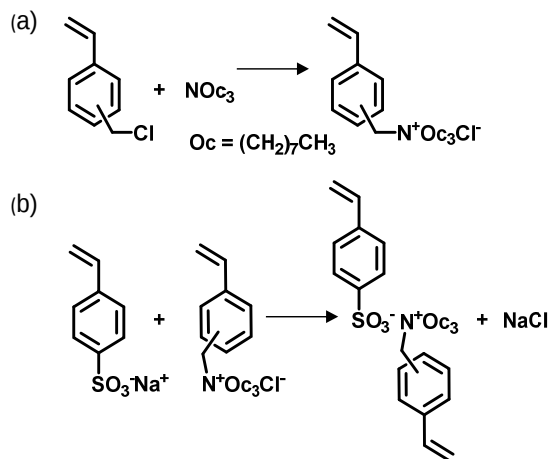


Figure 3. Synthesis of (a) vinyl benzyl tri-*n*-octylammonium chloride and (b) vinyl benzyl tri-*n*-octylammonium styrene sulfonate (VBTOA-SS).

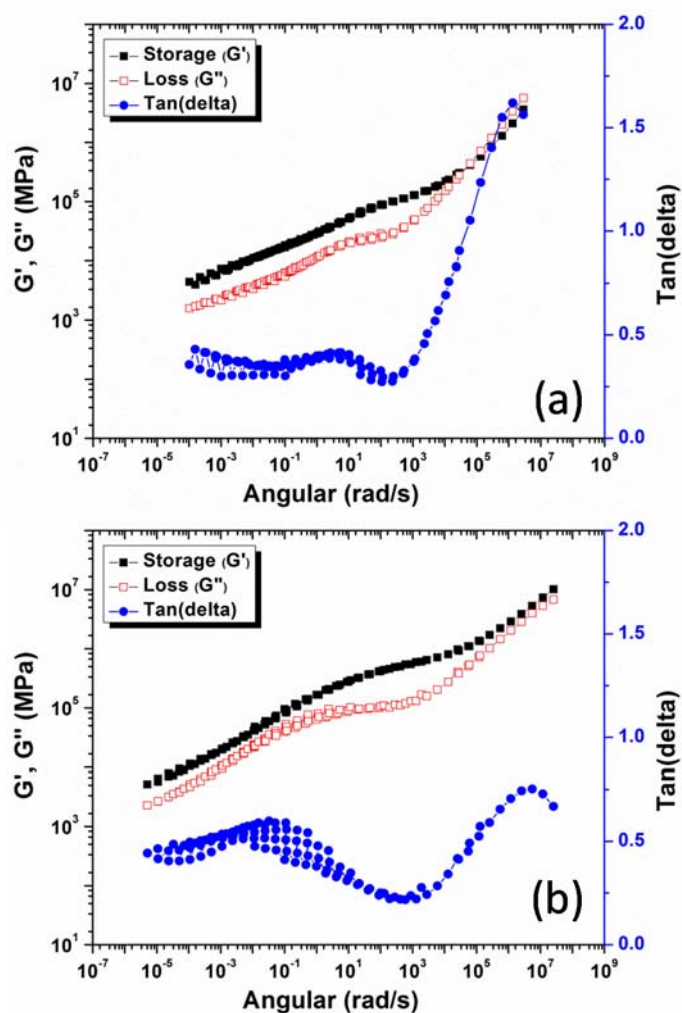


Figure 4. Master curves for PBA crosslinked with (a) 1 mol% and (b) 3 mol% VBTOA-SS. Measurements made from -30 to 170 °C with a $T_{\text{ref}} = 30$ °C.

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