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Easily Processed Host-Guest Polymer Systems with High-T_g Characteristics (First-year Report)

by J. A. Orlicki, R. Hoffman, and P. Costanzo

ARL-MR-0819 **May 2012**

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14. ABSTRACT

A series of polymethylmethacrylates (PMMAs) were prepared with varying quantities of Diels-Alder (DA) crosslinks. The DA linkages are broken at elevated temperatures and may re-form at lower temperatures, which allowed the thermally responsive PMMA (TR-PMMA) to be blended with PMMA and melt processed on a laboratory scale twin-screw extruder. The blends were easily processed at elevated temperatures, although the initial level of DA crosslinkers included in the TR-PMMA backbone were insufficient to regenerate crosslinks. Higher levels of DA crosslinked TR-PMMAs have been prepared, and are being explored for DA bond reformation and mechanical behavior. In addition, the preparation of host-guest systems incorporating chromophores has been demonstrated, which will allow the use of the TR-polymer concept for electro-optically active polymer applications.

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1. Objective

The Army has interest in electrically driven, room-temperature terahertz (THz) sources, both continuous wave (CW) and pulsed, operating between ~0.3 and 3 THz. Key applications of interest for THz and ultrafast electronics include battlefield remote sensing of biological agents, chemical agents, and explosives (such as RDX and TNT). Additionally, the technique could have far-reaching application in the development of ultra-wideband sensing and communications. One of the primary hurdles in the maturation of the technology is material limitations. Polymer/chromophore systems are excellent candidate materials for THz emission/detection, although a polymer host must be able to contain the poled (aligned) chromophore within a robust, transparent, and chemically stable matrix in a manner such that the effective electro-optical coefficient is maximized. Unfortunately, relaxation of the chromophore in the host polymer leads to diminished lifetimes of the THz generation properties. The obvious route to improve alignment lifetimes is to use a high-T_g polymer as a host, but the processing temperatures required for high-T_g polymers can lead to chromophore degradation.

This project seeks to demonstrate and develop melt-processable materials with reversible crosslinks, with the goal of preparing materials which have characteristics of high-T_g materials yet allow for processing using moderate temperatures. The ultimate goal is to prepare host-guest materials for THz and optoelectronics applications that exhibit long lifetimes of aligned molecules hosted in the matrix.

2. Approach

The envisioned system depends on the identification of a thermally labile bonding group that can form robust bonds at lower temperatures. This is achieved through the use of Diels-Alder (DA) chemistry (*1, 2*). As shown generically in figure 1, a diene is attacked by a dienophile to form a ring structure. The formation of the ring structure is temperature dependent and reversible. For the current study, the widely studied furan-maleimide system was employed, which yielded a ceiling temperature of ca. 90 °C.

In addition to the synthesis of polymers functionalized with DA crosslinks, we investigated the processing of the polymers using our lab-scale DSM Xplore twin-screw compounder. This enabled the preparation of blends with virgin poly(methyl methacrylate) (PMMA) to post-synthetically control crosslink density and allowed for the introduction of chromophores. Chromophores may ultimately be oriented (or poled) in the film to provide opto-electronic materials with anisotropic behavior. Figure 2 illustrates the desired system in diagram form.

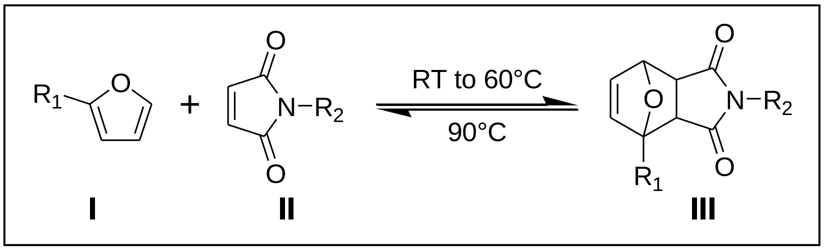


Figure 1. A thermally reversible DA adduct (III) is formed when a diene (I, furan) is combined with a dienophile (II, maleimide).

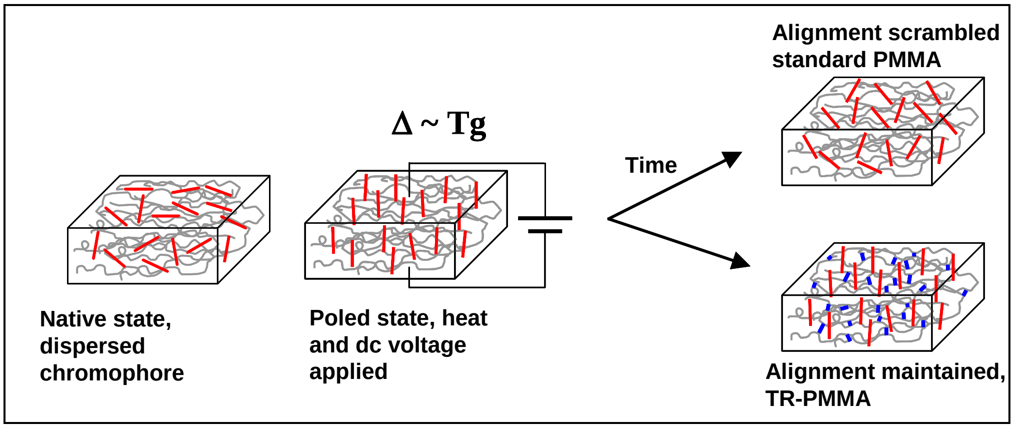


Figure 2. Schematic of chromophore poling and impact of thermally reversible crosslinking. The crosslinks (lower right) represent DA linkages, which should inhibit chromophore relaxation and extend alignment lifetime.

3. Results

3.1 Synthetic Efforts

Initial synthetic efforts targeted three different, thermally responsive (TR) crosslinkers (figure 3). While the linkers all incorporated the same maleimide-furan DA group, the polymerizable groups were varied to include (1) dual methacrylate groups, (2) one methacrylate and one acrylate, or (3) both acrylate groups. The polymerizable units allowed for the incorporation into PMMA chains through free-radical polymerization.

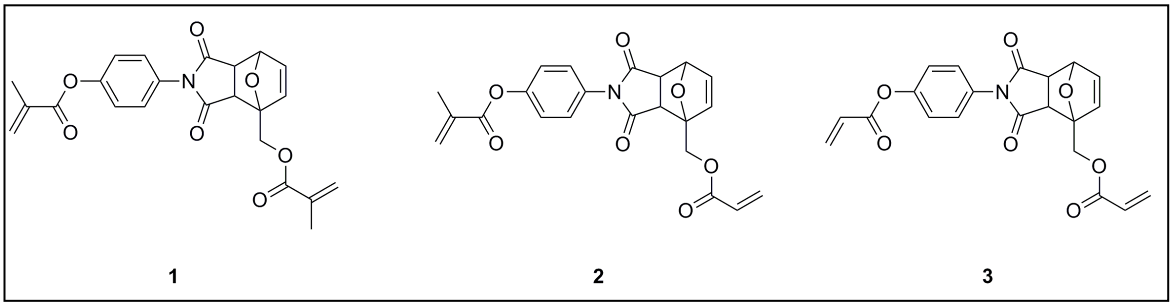


Figure 3. TR DA-based crosslinkers.

Methyl methacrylate (MMA) and a TR crosslinker were polymerized into a TR PMMA. A variety of reaction conditions were explored to determine the maximum content of DA linkages to be incorporated into the material, as well as reaction time and scalability. In general, the methacrylate-functionalized crosslinkers reacted more readily than the acrylates with the MMA, resulting in faster gelation of the polymerization media and relative ranking of reaction rates of **1** > **2** > **3**. Differential scanning calorimetry (DSC) analysis of preliminary materials (figure 4) displayed the expected endotherm as well as a small shift in the T_g of the material. The endotherm is visible in the first cycle (blue trace), and is taken as the deviation from horizontal of the thermogram, starting at ca. 110 °C and peaking at ca. 150 °C.

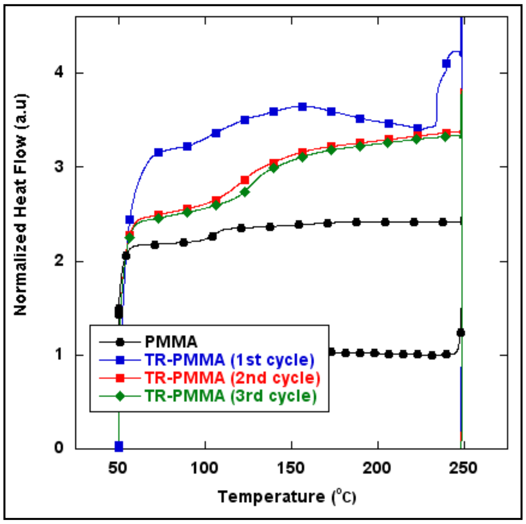


Figure 4. DSC analysis of TR-PMMA.

Three materials were scaled up to approximately 250-g batches and delivered to the U.S. Army Research Laboratory (ARL) by Costanzo. The polymers delivered consisted of PMMAs containing both 0.5% and 1.0% crosslinker 3, and 0.5% crosslinker 2. There were limitations to the initiation and polymerization system, and elevated levels of incorporation of the DA linkages (e.g., crosslinks) led to intractable material. Even at relatively low levels of TR-crosslink incorporation, the TR-PMMA was intractable and preparation of a well-dispersed material (e.g., powdered precipitate) was not practical.

Therefore, a new methodology had to be developed to generate a TR-crosslinked polymer. Here a TR additive was created that would aid in plasticizing the matrix at elevated temperatures and then increase crosslink density via DA linkage formation when thermal treatment was removed (figures 5 and 6). This molecule would not crosslink until after thermal treatment so initial blending would be vastly improved.

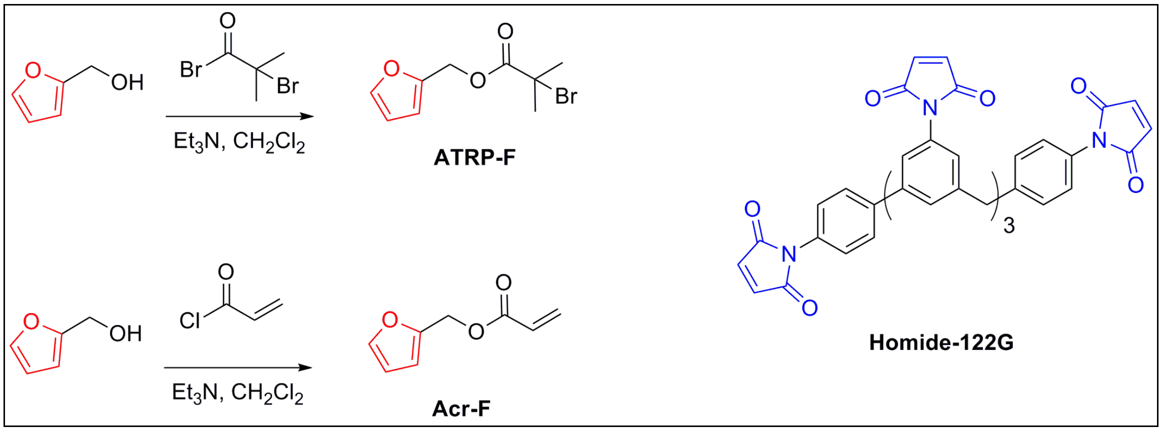


Figure 5. Scheme 1: Synthesis of an initiator for atom transfer radical polymerization functionalized with a furan atom transfer radical polymerization (ATRP)-F and an acrylate-furan Acr-F, monomer; structure of Homide-122G TR-crosslinker.

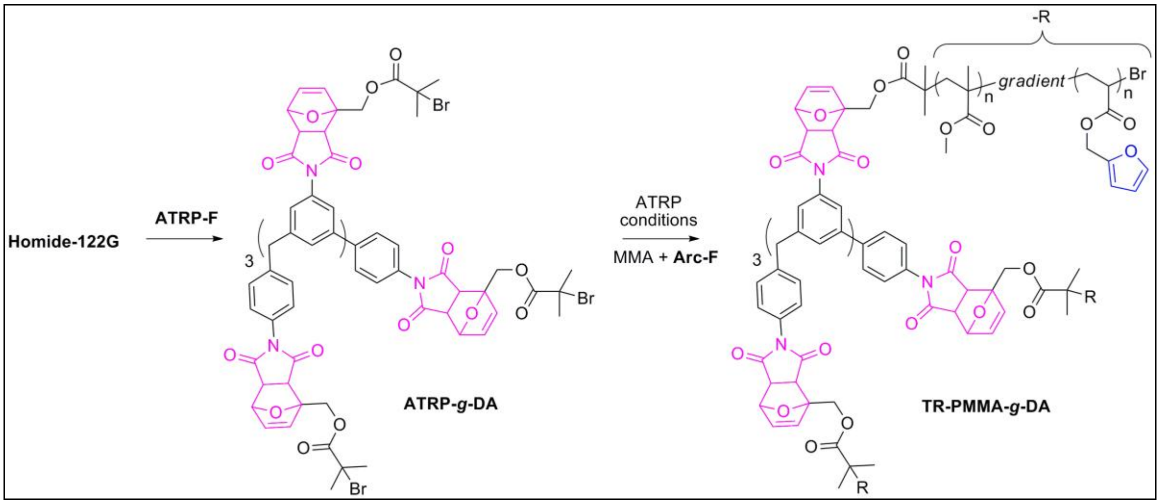


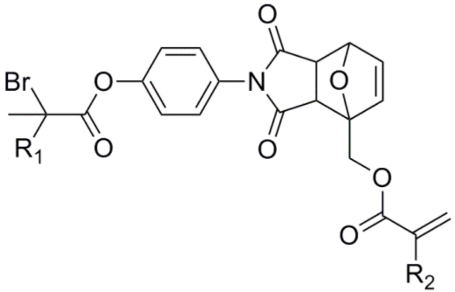
Figure 6. Scheme 2: Synthesis of TR-PMMA-g-DA.

Scheme 1 outlines the preparation of the small molecule precursors and the structure of the poly(maleimide) backbone (Homide-122g). Scheme 2 demonstrates the synthesis of TR-PMMA-*g*-DA, which has been completed, as well as material scale up.

In this experiment, TR-PMMA-*g*-DA serves to disrupt chain entanglement due to its brush structure. At elevated temperature, the side chains are cleaved, resulting in significantly lowering the molecular weight of the polymer, which should plasticize the matrix and lower the T_g. Upon cooling the material, DA linkages should reform, and by placing furan functionality along the backbone of the PMMA side chain, inter-chain crosslinking can occur, crosslinking the matrix.

Synthesis of the material was straightforward and efficient. Unfortunately, this material did not perform the retro-DA reaction. Therefore, a new TR molecule was identified for evaluation.

Figure 7 illustrates the inimer employed for the synthesis of hyperbranched TR-PMMA. This molecule serves as both an initiator and a monomer, thereby creating a branched topology when copolymerized with MMA. By selecting the appropriate R_1 and R_2 functional groups, one can control the rate of polymer chain growth from the initiator site as well as the rate of incorporation of the TR site in the backbone of the PMMA. Inimers 4–7 have been synthesized and polymerized to prepare materials. Further evaluation including analysis of the thermally responsive behavior of these polymers is currently underway. Additionally, the inimer strategy allows for easy variation of the composition of the matrix material. Future work will also explore the acrylate- and styrene-based backbones.



Sample	**R_1 (Initiator)**	**R_2 (Monomer)**
4	**H**	**H**
5	**H**	**CH_3**
6	**CH_3**	**H**
7	**CH_3**	**CH_3**

Figure 7. Synthesis of hyperbranched TR-PMMA.

3.2 Materials Evaluation and Processing Study

As part of the research efforts, a student from California Polytechnic University at San Luis Obispo worked over the summer in ARL's Weapons and Materials Research Directorate (WMRD) labs. The student, Christopher Roland, was a B.S./M.S. student from the Costanzo group, and he continued synthetic studies while here he also explored the physical properties of the TR-PMMA materials. He arrived with a significant amount of lightly crosslinked polymer, represented by compositions A–C in table 1 (note that X-linker correlates to molecules from figure 3). He also brought with him some precursor maleimide material, which was used to produce additional TR crosslinker while at ARL, which fed into our preparation of more highly crosslinked polymers (compositions D–G). Preparation of the polymers followed the initial procedure elucidated in the previous section. Higher levels of crosslinking were obtainable at ARL due to our ability to process intractable materials using thermoplastic processing equipment.

Table 1. TR-PMMA compositions by crosslinker loading.

Polymer	X-linker	Wt% TR-XL	Mol% TR-XL
A	2	0.5	0.25
B	3	0.5	0.25
C	3	1.0	0.5
D	3	2.5	1.28
E	3	5.0	2.60
F	3	11.0	5.89
G	3	56.2	39.39

The polymers were analyzed with DSC to determine T_g and to measure the retro-DA endotherm. Attempts were made to characterize molecular weight of the polymer with gel permeation chromatography, but efforts to solubilize the crosslinked polymer were not entirely successful. In short, a ca. 100-fold excess of furfuryl alcohol was refluxed with the crosslinked polymer in toluene (bp ~105 °C, higher than retro-DA temperature) in an attempt to block the crosslinked polymer and free the chains for individual analysis. However, the polymers never fully dissolved, which prevented their analysis by gel permeation chromatography (GPC). Instead, the swollen polymers were analyzed using standard proton nuclear magnetic resonance (NMR) techniques, although molecular weight was not able to be determined.

^{1}H NMR spectra obtained from polymer G (highest x-link density) swollen in deuterated dimethylsulfoxide. The first spectrum was as-polymerized, while the second was subjected to heating in the solvent, which promoted the retro-DA reaction. Even in the hot solvent the polymer never fully dissolved, suggesting the possibility of side reactions (inter-chain transfer), which may have led to less thermoplastic behavior than anticipated. However, evidence of the retro-DA reaction is present and is shown by the decreased intensity of minor resonances at 3.0 and 3.25 ppm. These correspond to the bridgehead protons in the DA adduct. These peaks diminished and were replaced by alkene resonances at 5.2, 7.6, and 7.7 ppm from the furan and maleimide.

The polymers were ultimately evaluated for compatibility with thermoplastic processing conditions, represented by the DSM Xplore lab-scale twin-screw compounder (figure 8). This system uses two conical screws combined with a recirculating track to simulate long retention times on industrial compounding equipment while requiring very modest quantities of polymer. A maximum-capacity sample requires ca. 15 mL of volume to fill the screws and recirculation path. As a general procedure, the system was initially purged with a known quantity of virgin PMMA (Acrylite H15 from Amco Plastics) with the barrel temp at 230 °C, which was used to clean out any residue from previous runs or cleaning processes. The purge was collected and a mass was determined, providing a measure of remaining PMMA in the system. With a net target mass of ~15 g, the desired amount of virgin PMMA and TR-PMMA were added to the barrel and the feed-throat was closed. After recirculating ~15 min at 100 rpm, the polymer was extruded as a rod or was introduced into the DSM Xplore’s transfer line to allow for injection molding.

Figure 8. DSM Xplore lab-scale compounder (left); twin-screw compounding section with recirculation path (right).

In many instances, the inclusion of the TR-PMMA caused an increase in viscosity of the system relative to the virgin PMMA. This was primarily manifested as surface defects in injection molded parts, which exhibited a processing defect known as shark-skinnning. This defect is typically introduced into a system when a polymer melt exhibits a stick-slip motion at the dye wall. As we have little control over injection speed with our injection system, we also explored the use of compression molding techniques to prepare sample plaques for optical testing. Compositions of the processed formulations are shown in table 2.

While the majority of the TR-PMMA’s were successfully processed, they were certainly more viscous than the virgin PMMA. This was manifested in both an increase in down-force recorded during the processing run, as well as by increased current draw from the drive motor, which is a qualitative indicator of resistance to flow. The down-force measurement is obtained from a force transducer at the bottom of the extruder barrel, and the force obtained is a combination of barrel loading (how full the screws are) and the polymer melt’s resistance to flow. A highly viscous material at comparable loading equates to a higher viscosity. In some instances the down-force limit was reached before the blend was able to achieve full speed (100 rpm). In these instances the polymer was processed at 50 rpm. Figure 9 shows the down-force data recorded for three processing runs and demonstrates that even at moderate TR-crosslink loading (10%), the melt maintains processability under standard PMMA process conditions.

Table 2. Composition and optical properties of TR-PMMA blended plaques.

Sample	TR-PMMA	wt% TR-PMMA	Transmission	Haze	Clarity	Chrom.
I	NA	0.00%	90.60	5.11	92.60	x
II	**B**	19.96%	90.80	5.29	92.30	x
III	**B**	20.54%	89.30	16.30	84.90	x
IV	**B**	38.60%	86.20	6.70	89.50	x
V	**C**	19.44%	87.60	18.10	57.10	x
VI	**C**	40.29%	79.10	32.40	36.50	x
VII	**B**	67.12%	74.30	23.50	88.60	x
VIII	**C**	66.03%	79.60	44.10	42.40	x
IX	**A**	18.36%	86.00	9.89	76.20	x
X	**A**	38.23%	81.30	17.20	64.30	x
XI	**A**	57.66%	70.90	30.30	63.60	x
XII	**E**	19.08%	91.50	21.00	64.40	x
XIII	**D**	19.36%	90.10	6.46	82.80	x
XIV	**F**	19.46%	82.90	45.50	32.10	x
XV	**F**	39.21%	74.80	65.90	16.10	x
XVI	**D**	35.00%	90.50	9.56	77.50	x
XVII	**E**	32.31%	88.70	16.20	55.20	x
XVIII	**B**	56.60%	10.05	18.60	87.80	MNS
XIX	**B**	45.50%	23.40	24.70	78.70	MNA
XX	**C**	48.71%	26.50	29.90	64.00	MNS
XXI	**A**	50.35%	26.10	12.10	69.60	MNS

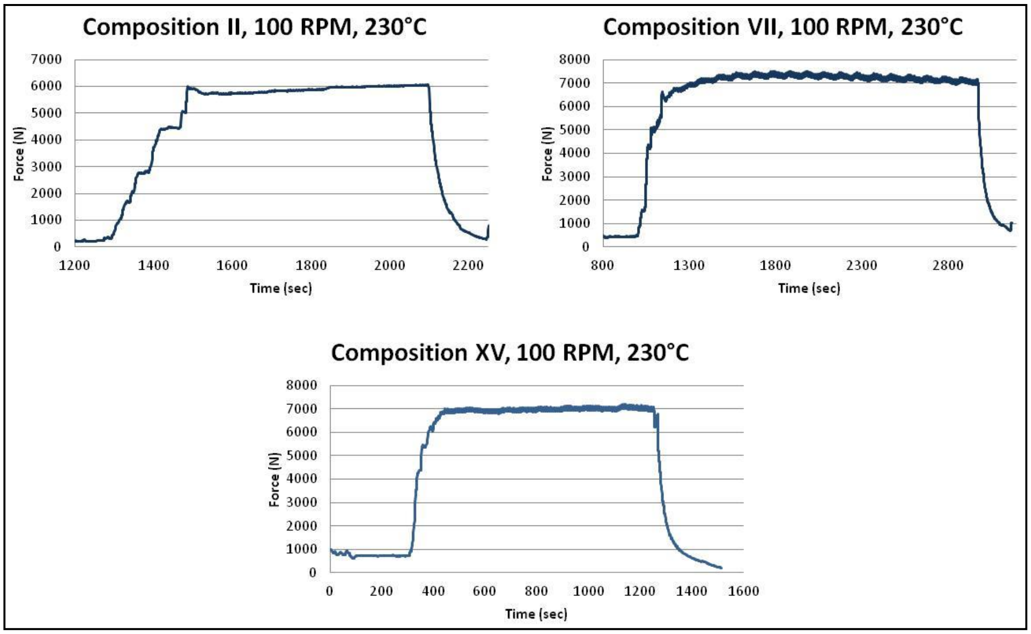


Figure 9. Down-force recorded during processing for indicated blends. Barrel temperature is 230 °C set to 100 rpm.

In addition to composition information, table 2 also includes optical property measurements performed on sample plaques. Plaques measured 1.5 in square with a depth of 0.0397 in (1 mm). These plaques were compression molded in-house using polished stainless steel facing plates (0.25 in thickness, McMaster) and window molds cut from aluminum stock (1 mm thickness, McMaster). Both facing plates and window molds were cut to specification using a computer-aided design (CAD)-driven water-jet cutter. For optical properties, transmission measures total light passing through the sample and a high value is desirable. Clarity measures light scattered less than 2.5° from the incident light and a low value is desired while haze measures the light scattered by more than 2.5° from the source light and a low value is advantageous. A picture of representative plaques is shown in figure 10.

Figure 10. Plaques of PMMA blended with TR-PMMA, corresponding to 0% (I, left), 21% (III), 39% (IV), and 67% (VII, right) TR-PMMA.

The polymer blends were subjected to various thermal and mechanical tests, including dynamic mechanical analysis (DMA) and DSC. DSC is frequently used to identify the T_g of polymeric materials and was used to investigate the reformation of DA linkages after the polymers had been processed. DMA was used to explore the impact of the TR-PMMA on the response of the polymer to heat and is probed by subjecting a polymer sample to an oscillatory load as the temperature is modulated. A plot of storage modulus vs. temperature is presented for blends I, III, and VII is presented in figure 11. No substantial shifts in modulus or T_g was observed by either technique for these samples, although sample VII showed some evidence of a broader thermal transition (note the extension of the transition region as the modulus changes from the glassy to rubbery plateau).

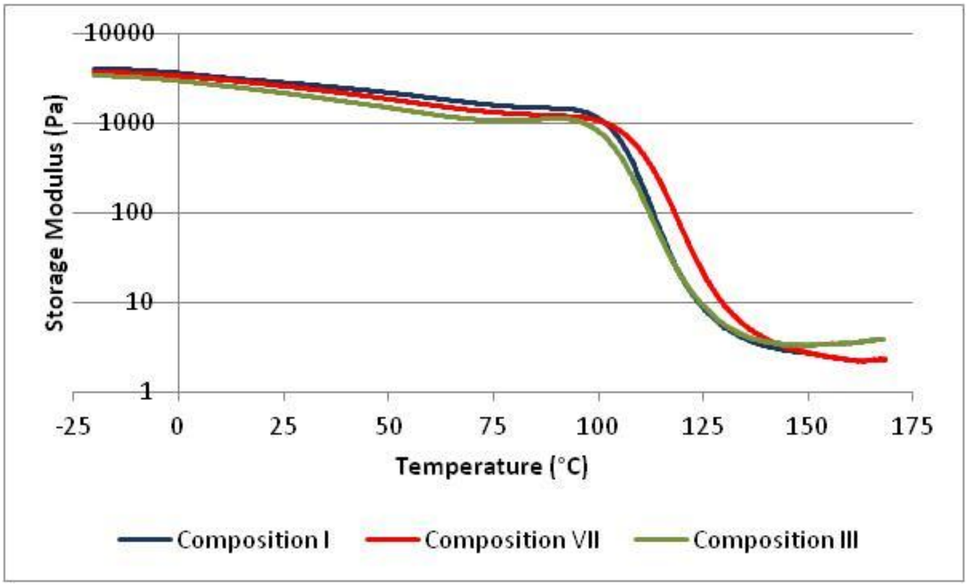
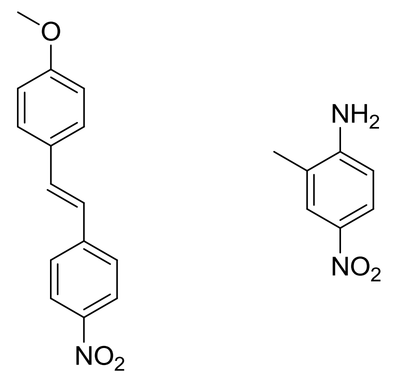


Figure 11. Storage modulus of PMMA blends.

DSC was employed to search for bond reformation in the blends. Unfortunately, there was little evidence for bond reformation, and no DA endotherm was found. This motivated the preparation of much more highly functionalized materials D-G, which were used to test the limits of processing capability. The lack of DA bond reformation, in retrospect, is not surprising. The TR-PMMAs only contained 0.5% wt/wt crosslinking monomers, which corresponded to an even smaller fraction of repeat units. Once broken, a furan functionality would need to be in close proximity to a maleimide group in order to re-form the DA linkage once the polymer cooled, and the small amount of DA crosslinks in the initial material meant that these interactions were rather infrequent. Analysis of extrudate XV (one of the highest TR-PMMA loaded samples that incorporated significant crosslinking) also showed no evidence of reformation of DA linkages after processing, although additional annealing steps have not been undertaken. The use of DA chemistry crosslinks in the self-healing materials literature suggests extended annealing may be required to achieve significant bond reformation (*3–5*). This also implies that aligning T_g of the material with the DA ring formation temperature might be most advantageous to achieve good levels of bond reformation. In limited studies with polymer G, we have investigated bond reformation at elevated temperatures of 40 and 50 °C over several days, and have observed modest levels of DA bond reformation. Polymer G has not yet been blended with normal PMMA, however.

In addition to blends with TR-PMMA alone, a pair of host-guest systems were explored, which incorporated virgin PMMA, TR-PMMA, and a small molecule chromophore. The chromophores selected included methoxynitrostilbene (MNS) and 2-methyl-4-nitroaniline (MNA), which are shown in figure 12. In both cases, blends were prepared with the resident virgin PMMA, combined with 10% total solids loading of the chromophore, and the balance contributed from 1% wt/wt crosslinker TR-PMMA.



Methoxy-nitro stilbene (MNS)

2-Methyl-4-nitroaniline (MNA)

Figure 12. Chromophore structures.

These materials processed easily due to plasticization from the chromophore. Both chromophores resulted in substantial red-shifted absorption compared to a sample prepared in virgin PMMA. We expect that this was caused by a potential ring-opening of some of the TR-PMMA maleimide with the free amine in MNA. The MNS could also participate in the DA reaction in the case of MNS; although, the alkene is not optimal for DA reactions, it is present in a high concentration relative to the furan functionality. To address these concerns, an alkylated version of the MNA chromophore is being pursued. While alkylation will alter the optical properties of the molecule slightly (causing a red-shift), generating a N,N-dialkylated product will prevent participation in any maleimide ring-opening side reactions, improving its utility in a DA-based system.

Detailed evaluation of the chromophore-containing materials is underway at the Adelphi Laboratory Center. The materials have been poled (e.g., aligned) under high voltage conditions and did not exhibit materials failures such as shorting/breakdown. They are being maintained at –10 °C while a new testing apparatus is being constructed, which will allow for the direct measurement of electro-optical coefficients at 830 nm via the method of Sandalphon et al. (*6*) and will therefore allow for the direct measurement of chromophore alignment in the guest-host system. This method is superior to the Maker Fringe method previously used, which only provided an indirect measurement of the electro-optical coefficient. Watching the decay of the alignment using the method of Sandalphon et al. over time will demonstrate the impact of the TR-PMMA on the lifetime of the host-guest systems.

3.3 Continuation Plan

Efforts are underway to complete the PMMA-related work in this project and transition to a polystyrene (PS)-based system. PMMA was initially selected due to the team's familiarity with the synthesis and processing of the material, but PS is more transparent in the THz signal range. To bring this work to a successful end, blends of the TR-PMMA and PMMA will be processed and formed into sample specimens for dynamic mechanical analysis. Performing a series of frequency and temperature sweeps will allow for the description of master curves for the materials, and permit the calculation of relevant shift factors. Annealing profiles will be developed for the PMMA materials to determine the required conditions for bond reformation.

For the PS-based materials, following synthesis and processing, plaques of the material will be provided to both Dr. Robert Hoffman at Sensors and Electron Devices Directorate (SEDD) and Professor L. Michael Hayden at University of Maryland Baltimore County (UMBC). Hoffman will be able to measure the electro-optical coefficients of the guest-host materials and track relaxation over time. Hayden will measure the TR-PS system for transparency in the THz regime and evaluate poled materials for THz applications.

4. Conclusions

A series of PMMAs were prepared, which incorporated various levels of DA crosslinking units to form TR-PMMA. These polymers were evaluated for their ability to be processed using thermoplastic processing techniques and were found to be fully meltable and moldable. When the DA linkages were incorporated at low loading (~1% wt/wt), the polymers did not exhibit a significant amount of DA bond reformation after processing. A series of more highly crosslinked materials have been prepared, and those have shown some level of DA bond reformation at elevated temperatures.

The TR-PMMAs were able to be blended and compounded with virgin PMMA, which diminished the light transmission through the polymer when compared to standard PMMA. Host-guest systems were also prepared, which incorporated electro-optically active chromophores into the PMMA/TR-PMMA blend. While successfully incorporated, the potential for side reactions between the DA components and the chromophores led to some color shifts. The guest-host systems were able to be poled (aligned) and did not exhibit material failures when subjected to the high poling voltage (ca. 50 kV), although the lifetimes of alignment have not yet been measured.

The first year of this project highlighted several hurdles to the practical application of thermally reversible crosslinks in thermoplastic systems, but all of the issues may be addressed through modification of our DA system and our intended chromophore.

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6. Transitions

This initial work was presented in poster form at the Western Coating Show in Las Vegas, NV, on 24 October 2011 by Chris Roland, who received 3rd place in the Outstanding Technical Poster Presentations contest.

List of Symbols, Abbreviations, and Acronyms

ARL	U.S. Army Research Laboratory
ATRP	atom transfer radical polymerization
CAD	computer-aided design
CW	continuous wave
DA	Diels-Alder
DMA	dynamic mechanical analysis
DSC	differential scanning calorimetry
GPC	gel permeation chromatography
MMA	methy methacrylate
MNA	2-methyl-4-nitroaniline
MNS	methoxynitrostilbene
NMR	nuclear magnetic resonance
PMMA	poly(methyl methacrylate)
PS	polystyrene
SEDD	Sensors and Electron Devices Directorate
THz	terahertz
TR	thermally responsive
UMBC	University of Maryland Baltimore County
WMRD	Weapons and Materials Research Directorate

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4	US ARMY RSRCH LAB ATTN IMNE ALC HRR MAIL & RECORDS MGMT ATTN RDRL CIO LL TECHL LIB ATTN RDRL CIO MT TECHL PUB ATTN RDRL SEE M R HOFFMAN ADELPHI MD 20783-1197