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Thermomechanical Synergisms from Ionic Liquid Doping of Poly(methyl methacrylate)

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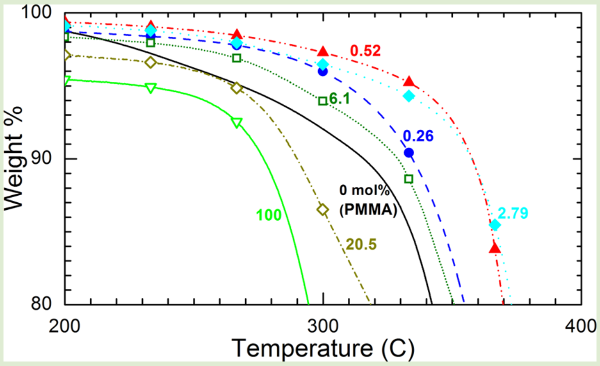
Supporting Information

ABSTRACT: A synergism between methyl methacrylate and an amphiphilic ionic liquid acrylate 1-(11-acryloyloxyundecyl)-3-methyl imidazolium bromide (IL) not only increases the apparent thermal stability (kinetic retardation of thermal decomposition) of poly(MMA-*co*-IL) copolymers by 50 °C at relatively low doping levels of 0.5 mol %, but also increases the storage (∼10%) and loss (15−25%) moduli over 0−75 °C (increasing the elasticity). Moderate to high doping levels provide plasticization without the risk of leaching or plasticizer contamination.



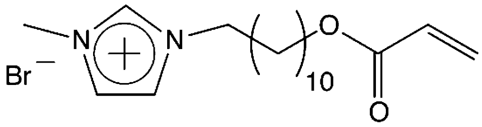
Poly(methyl methacrylate) (PMMA) is well-known to be susceptible to thermal depolymerization at the relatively low temperature of 220 °C.[1,2] The use of low molecular weight acrylate comonomers to "dope" PMMA and to thereby reduce and block the thermal unzipping of PMMA appears to be a widely known industrial practice.[3] Effects of alkyl acrylates on thermal and photooxidative degradation of poly(MMA-*co*-alkyl acrylate) have been extensively analyzed and reported.[4]

Ionic liquids are useful plasticizers for diverse engineering polymers, including poly(vinyl chloride) (PVC),[5] poly(ethylene oxide) (PEO),[6] poly(vinylidene fluoride) (PVDF),[7] poly(vinyl alcohol) (PVA),[8] and PMMA.[9,10] In these cases, the ionic liquids are dissolved in the polymer and are believed to function similar to other well-known plasticizers such as dialkyl phthalates in PVC.[11]

We used the acrylate 1-(11-acryloyloxyundecyl)-3-methyl imidazolium bromide (IL) as dopant or comonomer (Scheme 1). This imidazolium-based monomer and related monomers have been found to yield a variety of interesting materials.[12−21]

Bulk and solution copolymerizations of MMA and IL at various monomer ratios were examined, and we used TGA thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamical mechanical analysis (DMA), and size-exclusion chromatography (SEC) to evaluate the effects of IL as a comonomer on thermal stability, T_g (glass transition), mechanical moduli, and molecular weight. We found synergisms that include suppression of thermal unzipping at 220 °C at very low doping levels with concomitant extension of the high temperature degradation by 50 °C and increases in the storage and loss moduli over ambient temperature ranges.

Scheme 1. IL



Bulk polymerizations using AIBN thermal initiation, all at 60 °C, were done at IL levels of 1, 2, 5, 10, 20, 50, 75, and 100% (w/w) using NMR tubes as reaction vessels. Solids were easily recovered by careful fracture of the NMR tubes, and the rod sample morphology was convenient for double cantilever DMA analyses.

Thermal stability of the poly(IL-*co*-MMA) bulk copolymer samples was investigated by TGA. These rods were heated from 25 to 525 °C at a rate of 10 °C/min under a nitrogen atmosphere. There are two trends visible in the TGA data of Figure 1. As IL content increases, the onset of decomposition is shifted to higher temperature, up to 10% (w/w) IL. At higher doping levels the early decomposition of the IL monomer becomes increasingly apparent.

The 1% IL sample shows an approximately 15 °C increase in apparent thermal stability over the PMMA control as a shift in the thermal decomposition (10−90 wt%). This shift at 5% decomposition is a bit greater than 40 °C and it increases further for 2% IL, further still for 5% IL (65−67 °C), and

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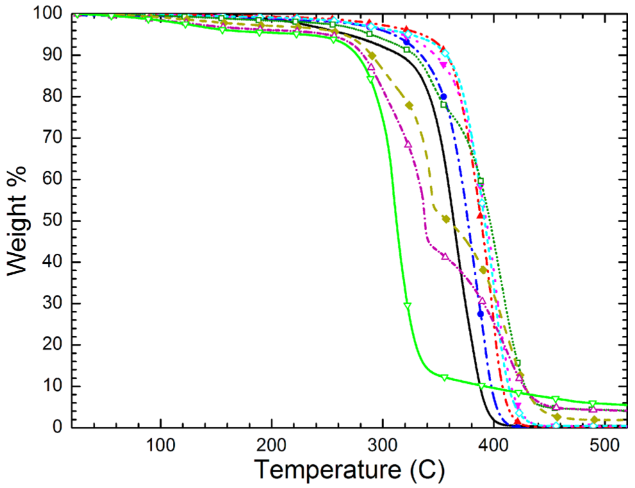

Figure 1. TGA of bulk polymerized copolymers, poly(IL-*co*-MMA) at various weight % IL: — (black; 0%); ● (blue; 1%); ▲ (red; 2%); ▼ (purple; 5%); ◇ (light blue; 10%); □ (green; 20%); ◆ (dark green; 50%); △ (purple; 60%); ▽ (light green; 100%).

decreases slightly for 10% IL. At 20−50% IL content, this onset of decomposition decreases dramatically with a sharp decrease below PMMA evident for the 50, 60, and 100% IL samples. The optimal doping level appears in the 2−10% (w/w) IL range.

The second trend present in the TGA analysis becomes apparent above 10% IL, where two distinct decomposition curves are observed for each of the copolymer samples. The PMMA and polyIL homopolymer rods yield curves exhibiting essentially a single decomposition process. TGA analysis of IL monomer showed a decomposition curve midpoint of approximately 300 °C (see SI), which is similar to that of the polyIL homopolymer decomposition curve (Figure 1). The bulk PMMA homopolymer rod shows a higher decomposition midpoint, roughly 365 °C, and the average midpoint for the 2, 5, and 10% (w/w) IL copolymers is about 391 °C.

These data also establish that polyIL is less thermally stable than PMMA. Therefore, the first segment in each of the copolymer sample decompositions above 10% IL can be assigned to decomposition of IL monomers and the second to MMA monomer decomposition. When taking the weight percent of IL residue remaining at 525 °C into account, the ratio of IL weight loss to MMA weight loss is in very close agreement with the weight ratio of IL to MMA present in the samples prior to polymerization.

Poly(IL-*co*-MMA) samples of up to 60% IL content were analyzed by DMA. The loss moduli are illustrated in Figure 2 (see SI for storage moduli). The storage and loss moduli show similar trends in magnitude over the −30 to 75 °C range. The 1 and 2% IL samples exhibit greater elasticity and loss than the PMMA control. The 5% IL sample essentially overlays the PMMA, and 10% and higher IL content samples steadily decrease in magnitude beneath the PMMA control values. This elastic (mechanical) synergism appears confined to doping levels less than 5% IL. The decreases in magnitude below the PMMA control values indicate de facto plasticizing by the softer IL components.

Both the PMMA and the IL-doped samples exhibit complex loss moduli. It is conventional to assign the highest temperature loss peak to the T_g, but all of the samples suggest the presence of additional relaxations consistent with second T_gs and a β-relaxation over −30 to 25 °C.

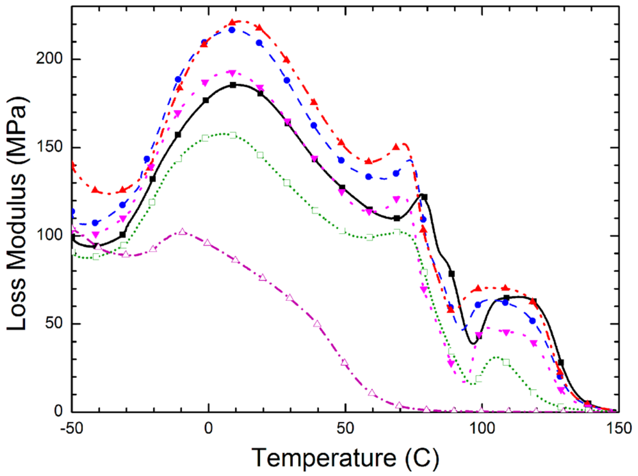

Figure 2. Loss moduli of bulk polymerized copolymers, poly(IL-*co*-MMA) at various weight % IL: — (black; 0%); ● (blue; 1%); ▲ (red; 2%); ▼ (purple; 5%); □ (green; 20%); △ (purple; 60%).

The T_g values suggested by the higher temperature peaks in Figure 2 are quantitatively different than but consistent with a series of T_g measured by DSC (see SI for DSC scan data). The T_g values estimated for these bulk polymerized samples from DSC scans are listed in Table 1. The PMMA control exhibits a very broad high temperature peak centered around 115 °C. The 1, 2, and 5% IL samples also exhibit very broad high temperature peaks centered around 110 °C, and the 20% IL sample exhibits a peak centered around 105 °C. Second T_g values are also exhibited by all of these sample rods, at 80 °C (PMMA) and at 70−75 °C for the 1−20% IL samples. These values compare surprisingly well with the highest temperature T_g values listed in Table 1. Agreement between second T_g values is moderate for PMMA and less so for the IL doped samples, but qualitative agreement persists. The DSC T_g of 40.9 °C for the 60% IL sample coincides with the shoulder in the loss curve at about 42−43 °C.

Table 1. T_g for Bulk and Solution Polymerized poly(IL-*co*-MMA) Copolymers (Determined by DSC)

	T_g (°C)	
IL (wt %)	bulk	solution
0	65.7, 113	73
1	59.5, 115	100
2		108
5	50.7, 115	
10	58.2, 110	
20	37.6, 105	70
50	36.6	40
60	40.9	
100	−26.7, 48.2	

The existence of multiple T_gs in various samples may indicate components of different tacticity or partially phase separated domains in the case of homopolymers. We see for both bulk homopolymers in Table 1 that multiple transitions exist for each. In the case of PMMA, this double transition behavior may be assigned to the distinctive double-humped molecular weight distribution obtained during bulk polymerization (effects from homopolymers of different molecular weight).[22,23] The lower T_g component may be assigned to one having predominantly isotacticity, and the higher component may be assigned to one that is mainly syndiotactic.[24,25] In the case of polyIL, the distinctively different low and high T_g values may be assigned to structures yet to be characterized, except by DSC and DMA, but one is most likely due to an "ionomer effect" (see sequel). The presence of hydration water in this homopolymeric material, we believe, is secondary to the ordering role of the undecyl tethers and the dipolar effects of the imidazolium bromide ion pairs. The existence of two T_gs for the copolymers is corroborated also by both DSC and DMA measurements. The existence of two T_gs in ionomers has been well documented in early studies.[26,27]

Copolymerization parameters for IL and MMA have not been measured, but related MMA/DA (dodecylacrylate) reactivity ratios r_{MMA} ($k_{MMA,MMA}/k_{DA,MMA}$) and r_{DA} ($k_{DA,DA}/k_{MMA,DA}$) in MMA-DA copolymerizations are about 3 and 0.38, respectively.[28] Further, reactivity ratios r_{MMA} and r_{ac} of 2.7 ± 0.6 and 0.32 ± 0.11, respectively, have been determined by analysis of a mixture of methacrylate/acrylate pairs in copolymerization.[29,30] The impact of the very high acrylate homopolymerization propagation rate is not seen in copolymerization until low mole fractions of MMA are in the available monomer pool. Such values argue against de facto block formation, especially at the low doping levels examined here.[31]

Light cross-linking was encountered in all of the (IL-*co*-MMA) copolymer rods produced by bulk polymerization, and this prevented molecular weight analysis by SEC because the required solubilization could not be obtained. This cross-linking has been tentatively assigned to a 1,3-bis(11-acryloyloxyundecyl)imidazolium bromide side product of IL synthesis.[15,16] Solution thermal polymerization was done in an effort to see if a series of copolymers could be produced that would dissolve in a suitable solvent for molecular weight analysis, such as DMF. Such polymerizations in DMF were successful (see SI for procedures).

TGA analysis was performed on a series of the copolymer compositions including PMMA as a control and 1, 2, 50, and 100% IL (Figure 3). As seen in the TGA data for the bulk copolymer rods (Figure 1), thermal stability initially increased compared to PMMA as IL content increased. The 1 and 2% IL samples at 10% decomposition are 65 °C to the right of the PMMA and about 27 °C higher than PMMA at 50% decomposition.

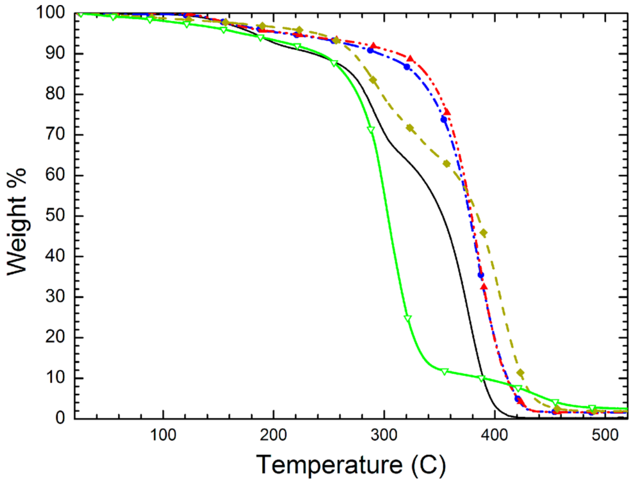

Figure 3. TGA of solution polymerized copolymers, poly(IL-co-MMA) at various weight % IL: — (black; 0%); ● (blue; 1%); ▲ (red; 2%); ◆ (dark green; 50%); ▽ (green; 100%).

In contrast to these bulk copolymer data, increased stability was seen at 50% IL content relative to the PMMA control, and the 100% IL homopolymer overlies the PMMA results over the first 10% decomposition. Solvent retention in the dried samples ranged from 2 to 4%, with polyIL retaining the highest amount. All of the solution polymerized samples degraded more substantially at lower temperature in these scans than did the bulk polymerized samples. We can assign this difference mainly to packing differences between these two set of samples.

These relative TGA stabilities for the solution samples are also consistent with T_g values measured by DSC (Table 1). The highest T_g values are lower for the solution polymerized samples in comparison to the bulk polymerized results.

These solution polymerized samples were suitable for molecular weight analysis by SEC, and they were dissolved in DMF for analysis (see SI for details). Molecular weight results are given in Table 2. This solution polymerized poly(IL-*co*-MMA) copolymer series showed a relatively uniform set of molecular weights, around 100000 Da, until IL content reached 75% (w/w). At this point, M_w falls to 55250 Da. The IL homopolymer M_w is even smaller at 27950 Da.

Table 2. SEC Molecular Weight Analysis of Solution Polymerized Poly(IL-*co*-MMA) Copolymers

IL (wt %)	M_n (Da)	M_w (Da)	M_z (Da)	(PDI)
0	50450	98150	159500	1.95
1	32050	92000	159000	2.87
2	28950	85100	151500	2.94
5	50150	97050	159000	1.94
10	41950	99750	176500	2.38
20	20900	89600	180000	4.29
50	35390	116000	302500	3.28
75	9340	55250	145500	5.92
100	9360	27950	144500	2.99

The data in Figure 1 show that water retention at IL doping levels less than 20% is negligible, but such retention is noticeable at 20% and higher. Similar insensitivity to water is illustrated in the data of Figure 3. Up to three water molecules per IL monomer unit can be retained; if not exhaustively dehydrated in vacuo, it appears no more than 1−1.5 water molecules of hydration are retained per IL in these studies. To the best of our knowledge, the PMMA blocks do not retain hydration water, and the only contact with water in these studies was with a very small amount of hydration water carried by the IL.

The 1 and 2% IL doping causes an initial increase in M_w/M_n polydispersity index (PDI) to about 3, while the PMMA PDI is about 2. The 5% IL sample exhibits about the same amount as the PMMA control, and further increases in IL lead to substantially higher PDI values. This increase in PDI and dramatic decrease in M_n have also been observed in SEC analyses[32] of solution-polymerized poly($ILBF_4$-*co*-MMA), where the $ILBF_4$ was a tetrafluoroborate salt instead of the bromide salt used in this study.

The increase in thermal stability at low doping levels of 2−5% by weight (0.5−1.3 mol %) is surprising. Although acrylate doping is practiced industrially to retard thermal unzipping of

PMMA, it also appears that higher temperature degradation processes are retarded by this imidazolium acrylate doping. While most of the MMA is lost by reversion to monomer and sublimation, the decomposition of acrylates is characterized by chain scission and decomposition of pendant ester groups.[4] Thermal analysis of poly(isobutylene-*co*-*p*-methyl styrene) copolymers functionalized with imidazolium bromide showed that thermal stability was improved significantly over the 200–350 °C range.[33] A sucrose-based cross-linker, 1′,2,3,3′,4,4′,6,6′-octa-*O*-allylsucrose, and related moieties imparted significant thermal stabilization without inducing increases in T_g when used to cross-link MMA.[32] The hypothesized stabilization mechanism involved tertiary protons alpha to oxygen, becoming active in chain transfer to produce, for example, allyl radicals that terminate unzipping polymer chains.[34]

A thermal stability study of MMA copolymers with methyl, ethyl, and butyl acrylates showed that increasing acrylate substitution (6–62 mol %) resulted in increasing thermal stability.[3] Each of these acrylate homopolymers is thermally more stable than PMMA, and so it is easy to understand how doping with such acrylates will tend to block thermal unzipping and produce segments with greater thermal stability.

The T_g values (Table 1) for both the bulk polymerized and the solution polymerized copolymers exhibit a slight to substantial increase, respectively, at low doping levels and cannot, therefore, satisfy the Fox equation. A T_g analysis of any series of imidazolium/MMA copolymers is not available, except for a companion study[32] of the tetrafluoroborate homologue of IL ($ILBF_4$). In that study, a significant increase in T_g was observed over the range of 1–20% (w/w) $ILBF_4$ doping in poly($ILBF_4$-*co*-MMA) and the Fox equation cannot be satisfied without introducing an interaction parameter. However, butyl vinylimidazolium/butyl acrylate copolymers were found to obey the Fox equation.[35] A significant difference between IL and $ILBF_4$ in comparison to vinylimidazolium-based polymers and copolymers is the presence of a significant tether between the imidazolium group and the backbone in the first class and none in vinylimidazolium polymers. This first class has many more degrees of freedom associated with how the imidazolium group can interact within a given chain and with separate proximal chains. Such interactions would make a good conformational energy study.

Small angle X-ray scattering (SAXS) was used to study structural changes in a series of poly(BVImBr-*co*-MMA) copolymers, and three structural details were resolved:[35] (1) the homopolymers and copolymers were amorphous; (2) the backbone–backbone separation produced a small scattering peak at a scattering vector value $q \sim 10\ \text{nm}^{-1}$ for PMMA and for 5% BVIm-doped PMMA (this backbone–backbone distance increased at high doping to $q \sim 4\ \text{nm}^{-1}$); (3) a peak attributed to π–π stacking (stacking of imidazolium rings) was resolved at high doping at $q \sim 16\ \text{nm}^{-1}$. We can expect that our copolymers also are amorphous and that similar to larger interchain backbone spacings exist, because the pendent undecylimidazolium bromide groups of our copolymers are significantly larger than the imidazolium bromide groups of the Green et al. study.[35] We do not have any direct evidence for π–π stacking in our copolymers, although such stacking might be present.

These low doping levels epitomize the definition of ionomers, and part of the moduli-increase effect at low IL-doping may be attributed to an "ionomer effect."[36] While relatively sparsely situated along the backbone, the imidazolium bromide groups at the end of undecyl tethers are free to undergo Coulombic and dipolar attractive and repulsive interactions. These interactions may be thought of as de facto interchain cross-links that provide additional thermal and mechanical cohesiveness and that make the materials thermoplastic elastomers. At doping levels beneath 10% by weight IL, we believe this "ionomer effect" is the most likely source of the increased mechanical modulus exhibited in this system as well as for the modest increases seen in T_g at low doping levels.[37]

It is known that ionic liquids plasticize a variety of polymers in a conventional way by forming miscible mixtures and lowering T_g values. It appears that moderate to high doping of PMMA by reactive comonomers, such as IL, can also plasticize, but in the present system, there is no possibility for blooming or for separation of the plasticizer from the bulk polymer. Reactive doping, therefore, appears an alternative approach to plasticization.

There is good empirical support to correlate this low doping thermal stabilization with elevated T_g values. The additionally unexpected increase in storage and loss moduli over temperature ranges below the T_g is consistent with chains that are more constrained from thermally induced excursions. Such thermomechanical synergisms would appear to merit more detailed chemical and mechanistic study, including more advanced calorimetric degradation, comonomer sequence distribution, and chain packing studies.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental materials, synthesis, and characterization methods and auxiliary TGA, DMA, and DSC results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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