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Synthesis and thermal properties of fullerene-containing polymethacrylates

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Summary

Three poly(methyl methacrylate-co-2-bromoethyl methacrylate) samples were prepared. The bromine groups in the copolymers were converted to azide groups followed by reaction with fullerene (C_{60}) to afford fullerene-containing polymethacrylates. The glass transition temperatures (T_gs) and heat capacity changes (ΔC_p) at T_g of these polymers were measured by differential scanning calorimetry. With increasing fullerene content in the polymethacrylate, the T_g value increases while the ΔC_p value decreases. The incorporation of fullerene improves the thermal stability of the polymethacrylate as shown by thermogravimetric analysis.

Introduction

Since fullerene (C_{60}) became available in large quantity (1), various methods to chemically modify the fullerene have been reported in the past few years. In order to improve the solubility and processability of C_{60}, and to obtain novel materials which make use of the attractive properties of C_{60}, many types of C_{60}-containing polymers have been prepared by the attachment of C_{60} as a side chain to preformed polymers or by the inclusion of C_{60} in the main chain. However, due to the identical physical environment of each carbon atom on C_{60}, a major problem during the synthesis is how to prevent crosslinking. Manalova et al. (2), Geckeler and Hirsch (3), and Patil et al. (4) attached C_{60} to soluble amino polymers by the amine addition to C_{60} double bonds. This method needs to control the C_{60} : aminopolymer ratio to obtain soluble products. However, there exists some multi-addition leading to insoluble products. Hawker (5) developed a new method to synthesize pendant chain fullerene-styrene copolymers using an addition reaction of azides to C_{60}. This method has the advantage that mainly mono(cyclo)addition occurs and so there is relatively little crosslinking. Another approach is to make use of the high reactivity of fullerene towards anions (6-9).

Poly(methyl methacrylate) (PMMA) is a general-purpose plastic. It is most often used because of its superior clarity and weatherability. Camp et al. (10) prepared C_{60}-containing PMMA through free-radical polymerization of MMA with C_{60}, but the product is star-like. In our study, we prepared "charm-bracelet" C_{60}-containing PMMA using

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Hawker's method. The thermal properties of these polymers were studied.

Experimental

C_{60} (99.9% purity) was obtained from Peking University, China, and was used as received. 2-Bromoethyl methacrylate was obtained from Polysciences, Inc. and was distilled at 56-58°C/5 mmHg before use. Methyl methacrylate was obtained from Fluka Chemie AG and was distilled under reduced pressure to remove stabilizer before use. PMMA was purchased from Aldrich Chemical Company, Inc.

Three poly(methyl methacrylate–co–bromoethyl methacrylate) [P(MMA-co-2-BEMA)] samples containing 0.76, 1.6, and 4.2 mol% of 2-BEMA were prepared by solution polymerization in methyl ethyl ketone at 70°C for 12 hr. using 2,2'-azobis(isobutyronitrile) (AIBN) as initiator. Br group was converted to N_3 group by reacting the copolymer with sodium azide in dimethylsulfoxide at 40-50°C for about 2 days. The product was allowed to react with C_{60} by refluxing in chlorobenzene until the strong IR band at 2095 cm^{-1} for the azide group had completely disappeared. Chlorobenzene was removed by rotary evaporation. The remainder was dissolved in tetrahydrofuran (THF) and the unreacted C_{60} was removed by centrifugation. The polymer solution was then poured into hexane to obtain crude C_{60}-containing polymethacrylate. The polymer was then redissolved in THF, centrifugated, and precipitated in hexane to obtain pure C_{60}-containing polymethacrylate.

UV spectra were obtained using a Hewlett Packard 8452A diode array spectrophotometer. NMR spectra were acquired using a Bruker AMX 500 MHz spectrometer. The glass transition temperatures (T_gs) were measured using a TA Instruments 2920 differential scanning calorimeter with a heating rate of 10°C/min. The initial onset of slope in the DSC curve was taken as T_g. Thermogravimetric analysis (TGA) was conducted in a nitrogen atmosphere using a TA Instruments SDT 2960 Simultaneous DTA-TGA. The nitrogen flow rate was 75 ml/min, and the heating rate was 20°C/min. GPC chromatograms were obtained with a Waters Millipore system using THF as eluent.

Results and discussion

Fullerene (C_{60}) and its derivatives exhibit a variety of outstanding electronic, conducting, photochemical and magnetic properties but their processability is poor (11). Therefore, soluble C_{60}-containing polymers have many potential applications. Various PMMA-C_{60} that we prepared are soluble in a variety of organic solvents such as THF, $CHCl_3$, acetone, etc. The polymers are brown and the color becomes deeper with increasing C_{60} content in the polymer.

Figure 1 shows the isothermal TGA curve of a PMMA-C_{60} sample in nitrogen at 450°C. The residue is taken as the C_{60} content of the sample. In contrast, PMMA completely degrades in 10 minutes at 450°C leaving no residue. It is known that C_{60} undergoes only minor weight loss up to 600°C (12), enabling the use of TGA to determine the weight percentage of C_{60} in the polymer (5). The three PMMA-C_{60} samples were found to contain 2.6, 7.4 and 13.5 wt% of C_{60}, or 0.4, 1.0 and 2.2 mol% of fullerene-functionalized methacrylate units, respectively. The mole percentage of fullerene in the polymer is less than that of the bromine in the parent P(MMA-co-2-BEMA), indicating that some of the fullerene molecules have reacted with two or more azide groups.

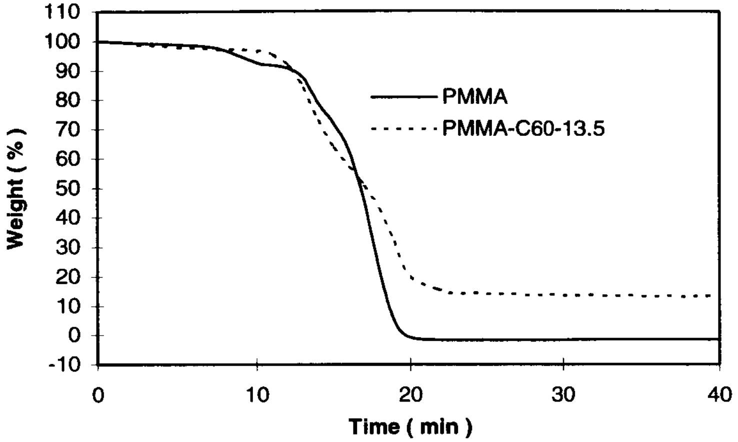

Figure 1. Isothermal TGA curves of PMMA and PMMA-C_{60}-13.5 at 450°C

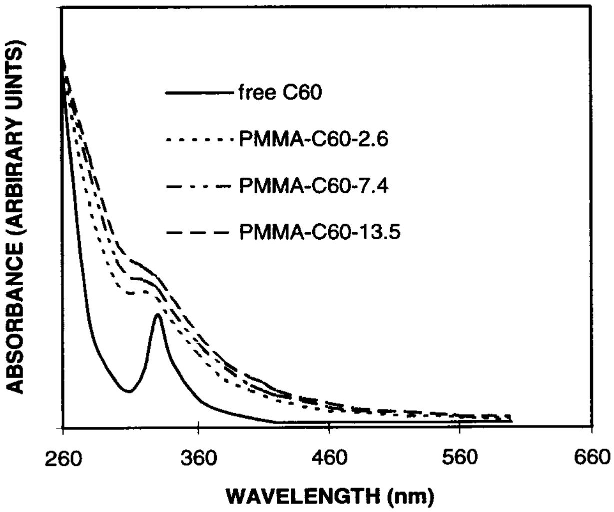

Figure 2. UV spectra of PMMA-C_{60} and free C_{60} in $CHCl_3$

Figure 2 shows the UV absorption spectra of PMMA-C_{60} and free C_{60} in $CHCl_3$. There is no absorption band above 260 nm for PMMA, and thus the absorption of PMMA-C_{60} in this region is entirely due to the incorporation of C_{60}. The absorption spectra of PMMA-C_{60} are very different from that of free C_{60} . The somewhat structured absorption band of free C_{60} is replaced by a decreasing curve with a shoulder at 330 nm, typical for substituted C_{60} (13).

The ^{13}C NMR spectra of PMMA-C_{60}-2.6 and PMMA-C_{60}-7.4 are essentially the same as that of neat PMMA. For PMMA-C_{60}-13.5, weak signals of fullerene in the region 130 ~ 155 ppm were observed. This is consistent with the results of other studies (5, 14).

As shown in Table 1, the molecular weights of the PMMA-C_{60} samples are higher than those of the parent P(MMA-co-2-BEMA) samples, providing further evidence of the incorporation of C_{60} in the polymer chains. However, the polydispersities of the PMMA-C_{60} samples are much broader than those of the parent polymer samples. Such an observation supports our earlier suggestion that some C_{60} molecules react with two or more azide groups.

The TGA curves of PMMA-C_{60} and PMMA are shown in Figure 3. Both PMMA and PMMA-C_{60} undergo a two-stage degradation. The amount of residue increases with increasing C_{60} content in the polymer. The incorporation of C_{60} improves the thermal stability of the polymer. The thermal degradation of PMMA is well understood (15). It degrades in two stages. The first stage is due to depolymerization initiated at unsaturated chain ends. The second stage is initiated by random chain scission to produce radicals which then unzip to yield monomer. The presence of the bulky fullerene rings apparently interferes with the chain scission and the unzipping process. As shown in Figure 4, the TGA curve of PMMA-C_{60}-13.5 is different from that of a physical mixture of PMMA and C_{60} containing 13.5 wt% of C_{60}, further showing the effect of the incorporation of C_{60} on the thermal stability of polymers.

DSC measurements showed that the incorporation of C_{60} significantly limits the motion of polymer chain segments and increases the T_g. On the other hand, the incorporation of C_{60} leads to an increase in the glass transition width (ΔT_g) and a decrease in the heat capacity change (ΔC_p) at T_g (Table 1). Distinct glass transition could not be observed for PMMA-C_{60}-13.5. Camp et al. (10) were also unable to detect T_g for their PMMA-C_{60} sample with a high C_{60} content.

In summary, C_{60} can be incorporated into polymethacrylate using poly(methyl methacrylate-co-2-bromoethyl methacrylate) as the starting material. The resulting PMMA-C_{60} samples are soluble in organic solvents. In view of the miscibility of PMMA with various polymers, the miscibility behavior of blends of PMMA-C_{60} will be investigated in our future studies.

Table 1. Characteristics of polymers

	M_n (kg/mol)	M_w (kg/mol)	T_g (°C)	ΔT_g (°C)	ΔC_p ($J \cdot K^{-1} \cdot g^{-1}$)
PMMA(Aldrich)	32.5	72.0	109	9	0.327
PMMA-C_{60}-2.6	32.3 (27.2)*	118.5 (49.4)*	132	12	0.237
PMMA-C_{60}-7.4	41.2 (36.2)*	160.9 (56.4)*	148	19	0.192
PMMA-C_{60}-13.5	23.1 (17.8)*	96.9 (34.5)*			

* Molecular weight of starting P(MMA-co-2-BEMA)

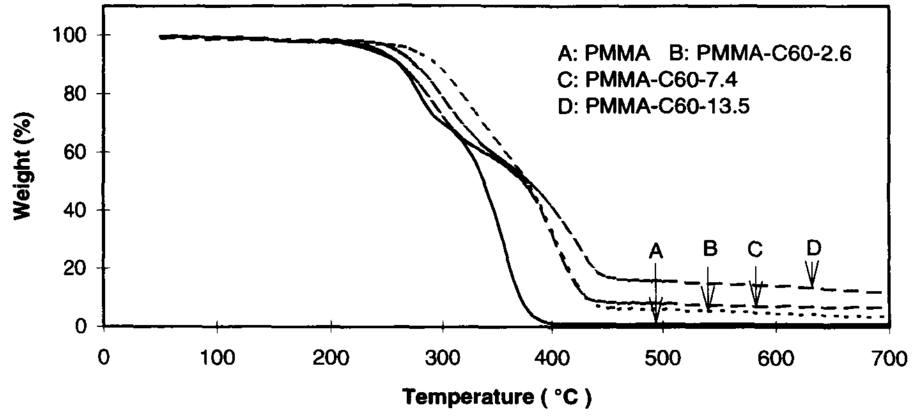

Figure 3. TGA curves of PMMA and various PMMA-C_{60} samples

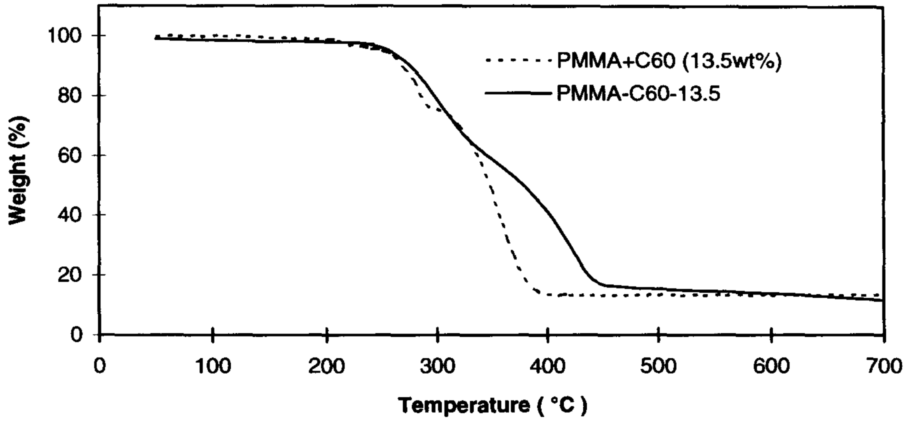

Figure 4. TGA curves of PMMA-C_{60}-13.5 and a physical mixture of PMMA and C_{60} containing 13.5 wt% of C_{60}

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