

Synthesis of fullerene-containing poly(alkyl methacrylate)s with narrow polydispersities

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Summary

Copolymers of allyl methacrylate with methyl methacrylate or *n*-butyl methacrylate were synthesized by group transfer polymerization. The pendant allyl groups of the copolymers were then hydrobrominated, followed by reaction with sodium azide. Fullerene was incorporated via an addition reaction of fullerene with azide group. The resulting fullerene-containing poly(alkyl methacrylate)s have fairly narrow polydispersities.

Introduction

Since methods for large-scale production of fullerenes were developed (1), fullerene-containing polymers have attracted considerable attention because the combination of fullerenes and polymers may give rise to useful materials with a variety of outstanding material properties (2-10). In general, there are three ways to synthesize polymers containing covalently linked fullerenes. One method is to copolymerize monomers directly with fullerenes (11-13). Another method is to functionalize fullerene to give a polymerizable monomer which is then polymerized or copolymerized (14,15). The third method is by "buckyball-fishing" which uses functionalized polymers to react with fullerenes (9,16). One of the "buckyball-fishing" procedures is to use azide group which has the advantage of reacting primarily with C₆₀ through mono-addition (17). We have earlier prepared C₆₀-containing polymethacrylates through reaction between azide-functionalized polymethacrylates and C₆₀ (18). The precursor polymethacrylates were obtained by copolymerizing methyl methacrylate and 2-bromoethyl methacrylate, followed by the conversion of bromide to azide group. The resulting C₆₀-containing polymethacrylates had broad polydispersity of 3.7-4.2. A C₆₀-containing polystyrene prepared by Hawker also had a fairly broad polydispersity of 3.12 (17). The broad polydispersities of these polymers are due to the polydispersities of the precursor polymers (around 2) and also the occurrence of multi-addition of azide with C₆₀. In this study, we have prepared azide-functionalized polymethacrylates from polymethacrylates containing pendant allyl groups. The allyl groups were incorporated into polymer by group transfer polymerization of allyl methacrylate with methyl methacrylate or *n*-butyl

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methacrylate. Thus soluble fullerene-containing poly(alkyl methacrylate)s with fairly narrow polydispersities were obtained.

Experimental

Materials

Methyl methacrylate, *n*-butyl methacrylate, and allyl methacrylate (all from Fluka) were all distilled under reduced pressure and dried and stored over molecular sieves before use. Tetrahydrofuran (THF) was refluxed over sodium and benzophenone, and distilled under nitrogen just prior to polymerization. Tris(dimethylamino)sulfonium bifluoride (TASHF₂) used was a 0.1M solution in acetonitrile. Fullerene (C₆₀ 99.9%, Peking University), sodium azide (Aldrich), methyl trimethyl-silyl dimethylketene acetal (MTS) (Aldrich), and all other reagents were used as received.

Characterization

Average molecular weights and polydispersities were determined by gel permeation chromatography with a Waters system consisting of a 600E pump, an external column oven of LC-100 set at 28°C, and a Waters 410 differential refractometer. The whole system was operated at a flow rate of 0.8 ml/min using THF as solvent. A calibration curve was constructed with polystyrene standards. Glass transition temperatures (*T*_gs) were determined on a DuPont 910 differential scanning calorimeter under nitrogen at a heating rate of 20°C min⁻¹. Thermogravimetric measurements were made with a TA Instruments 2960 simultaneous DTA-TGA under nitrogen at a heating rate of 20°C min⁻¹. 90 or 300 MHz ¹H-NMR spectra were recorded on a Jeol FX90Q or a Bruker ACF300 spectrometer in CDCl₃ solutions with tetramethylsilane as internal standard. FTIR spectra were recorded with a Perkin-Elmer 1600 or a Bio-Rad FTS165 FT-IR spectrophotometer. UV spectra were recorded on a Hewlett Packard 8452A diode array spectrophotometer with a Hewlett Packard Vectra QS/165 computer system.

Preparation of allyl group-containing polymethacrylate copolymers

In a typical procedure, MTS (0.10 ml, 0.5 mmol) was added to a magnetically stirred solution of TASHF₂ (0.02 ml, as a 0.1M solution in acetonitrile), allyl methacrylate (0.1 ml, 0.75 mmol) and *n*-butyl methacrylate (4.0 ml, 25.1 mmol) in 10 ml THF. The solution mixture was stirred for 3 h and then quenched by 2 ml methanol. The solution was poured into hexane and the resulting polymer was purified by re-precipitation from acetone solution into hexane twice and dried *in vacuo* at room temperature for 24 h. The yield was 81%.

Preparation of azide-substituted polymethacrylates

The copolymer (2.0 g) of allyl methacrylate with methyl methacrylate or *n*-butyl methacrylate was dissolved in 30 ml toluene. The solution was stirred and irradiated by a UV lamp (Blak-Ray longwave ultraviolet lamp of B100 AP UVP) for 3.5 h while dry hydrogen bromide was passed through the solution. The passing of HBr was continued overnight to complete the reaction, but without illumination. The

solvent was removed by evaporation under reduced pressure. The obtained polymer was purified by re-precipitation from acetone into hexane three times and dried *in vacuo* at room temperature for 24 h.

1.0 g of the above Br-containing polymer was first dissolved in 50 ml dimethylformamide (DMF) and then added with 60 mg sodium azide. The solution was stirred for 48 h at 50 °C and concentrated under reduced pressure, followed by precipitation in water/methanol mixture (9/1, v/v). This crude polymer was purified by re-precipitation from acetone to hexane and dried *in vacuo* at room temperature for 24 h.

Synthesis of C₆₀-containing Polymethacrylates

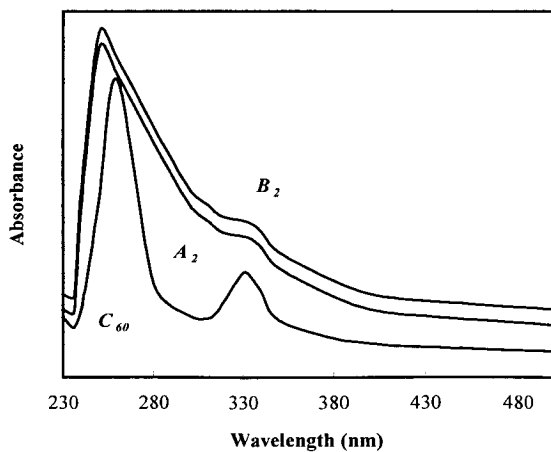
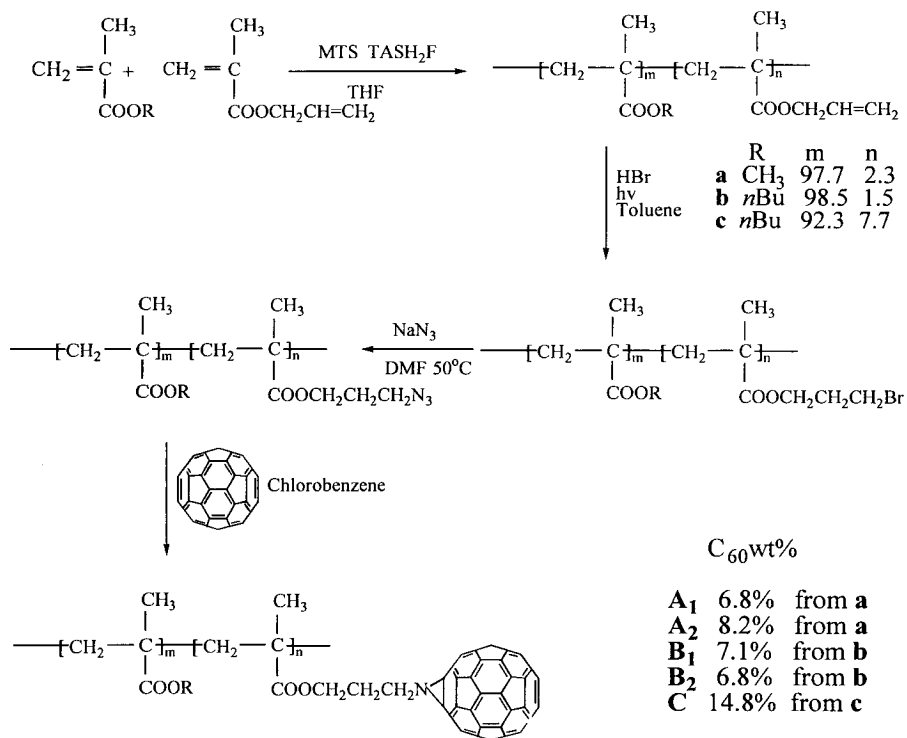
In a typical procedure, azide-containing polymethacrylate copolymer (300 mg) and fullerene (50 mg) were dissolved in 20 ml chlorobenzene. The solution was refluxed for 24 h under nitrogen and the solvent was then removed by evaporation under reduced pressure. The residue was redissolved in THF and followed by centrifugation to remove unreacted C₆₀ and insoluble cross-linked material. The solution was poured into hexane to re-precipitate polymer which was purified by further re-precipitation from THF into hexane several times and dried *in vacuo* at room temperature for 24 h.

Results and Discussion

The synthesis route is shown in scheme 1. Linear polymethacrylates containing reactive pendant allyl groups were synthesized by group transfer polymerization of allyl methacrylate and methyl methacrylate or *n*-butyl methacrylate using MTS as initiator and TASHF₂ as catalyst (19). The copolymer composition was determined by ¹H-NMR. ¹H-NMR spectra showed chemical shifts at $\delta = 4.4\text{--}4.5$ ppm for -OCH₂- groups, $\delta = 5.1\text{--}5.4$ ppm for =CH₂, and $\delta = 5.7\text{--}6.1$ ppm for =CH groups. FTIR spectra showed absorption of C=C at 1650 cm⁻¹ in addition to the absorption of C=O at 1750 cm⁻¹. After hydrobromination, the C=C absorption at 1650 cm⁻¹ disappeared. ¹H-NMR spectra showed a new signal at 4.1 ppm for -CH₂Br groups, and the signal of CH= at 5.8-6.0 ppm disappeared into the bulk -CH₂- hydrogens at 1.5-2.0 ppm while the signal of -OCH₂- groups shifted from 4.5 to 3.6 ppm.

Br-containing polymers reacted with sodium azide in DMF readily, resulting in azide-containing polymers. FTIR spectra showed that these polymers had an absorption at 2036 cm⁻¹ for -N₃ groups and ¹H-NMR spectra also showed chemical shift at $\delta = 2.8\text{--}3.0$ ppm for protons on -CH₂N₃ groups. Elemental analysis showed that the replacement of Br by azide group was complete quantitatively. Furthermore, the polydispersity of the polymer remained unchanged after hydrobromination and replacement reaction.

The progress of grafting of fullerene onto the polymethacrylates was monitored by infrared spectroscopy. After refluxing for 20 h, the color of the solution turned brown and the strong band at 2036 cm⁻¹ for azide group had completely disappeared. Then the solvent was removed by evaporation. The crude product was purified by repeated re-precipitation from THF into hexane. During the dissolution process, the THF-insoluble materials were removed by centrifugation. Purified C₆₀-

Scheme 1 Synthesis route of C₆₀-containing polymethacrylatesFig. 1 UV/Vis spectra of C₆₀-containing polymethacrylates and C₆₀ in chloroform.

containing polymethacrylates are brown or gray in color and their solubilities are similar to poly(alkyl methacrylate)s, being soluble in normal organic solvents such as THF, chloroform, and toluene. All the C₆₀-containing polymers show the characteristic IR absorption bands of C₆₀ at 520 and 1420 cm⁻¹.

The UV spectra of the C₆₀-containing polymethacrylates together with the corresponding spectrum of pure C₆₀ in chloroform are shown in Fig. 1. The spectrum of the C₆₀ on the polymer chain is different from that of the pure C₆₀. The peak at 330 nm in the polymer spectrum, attributable to C₆₀, is weakened to give rise to only a shoulder. This change clearly indicates that reaction indeed occurs between the azide-substituted polymethacrylates and C₆₀.

The C₆₀ contents of polymer were determined by thermogravimetry since the poly(alkyl methacrylate) backbone decomposes at 250-400°C but C₆₀ undergoes only minor weight loss up to 600°C.

Table 1. Synthesis of C₆₀-containing polymethacrylates from azide polymers

	Feed			C ₆₀ -containing Polymer				
	Azide polymer (mg)	C ₆₀ (mg)	Chloro-benzene (ml)	Yield (%)	C ₆₀ content (wt%)	M _w	M _w /M _n	T _g (°C)
A₁	500	72	20	71	6.8 (14.1) ^a	14800 (5200) ^b	2.3 (1.3) ^b	127 (99) ^b
A₂	500	130	200	81	8.2 (14.1) ^a	10600 (5200) ^b	1.4 (1.3) ^b	116 (99) ^b
B₁	300	50	20	55	7.1 (7.1) ^a	9200 (5500) ^b	1.3 (1.1) ^b	20 (17) ^b
B₂	555	85	100	91	6.8 (7.1) ^a	12000 (5500) ^b	1.5 (1.1) ^b	21 (17) ^b
C	100	72	20	67	14.2 (28.1) ^a	11400 (5400) ^b	1.3 (1.2) ^b	21 (20) ^b

a: theoretical C₆₀ content (see text)

b: value for precursor azide polymer

Table 1 summarizes the characteristics of various polymers. Polymers **A₁** and **A₂** can be considered as C₆₀-containing poly(methyl methacrylate) (PMMA) while polymers **B₁**, **B₂** and **C** are C₆₀-containing poly(*n*-butyl methacrylate) (P*n*BMA). Several salient points are noted from Table 1.

Firstly, the use of a dilute solution (A_1 versus A_2 and B_1 versus B_2) reduces the amount of insoluble materials, leading to a higher yield of the C_{60} -containing polymer. Apparently, the polymer molecules are further apart in a dilute solution, lessening the possibility of cross-linking reaction.

Secondly, the C_{60} contents of polymers B_1 and B_2 are close to the theoretical values based on the amounts of azide groups in the precursors and assuming mono-addition. However, for polymer C which is also a C_{60} -containing PnBMA as B_1 and B_2 , the C_{60} content is about 50% of the theoretical value. Therefore, at a higher azide content of the precursor polymer, there is an increasing chance of multi-addition. The result is similar to the previous reports (17,18) that the difference between the experimental and theoretical C_{60} content widens as the azide content increases. It is also of interest to note that for polymers A_1 and A_2 , there is a considerable extent of multi-addition in spite of the low azide content of the precursor polymer. The result suggests that when the pendent alkyl group is small, there is a greater chance for multi-addition.

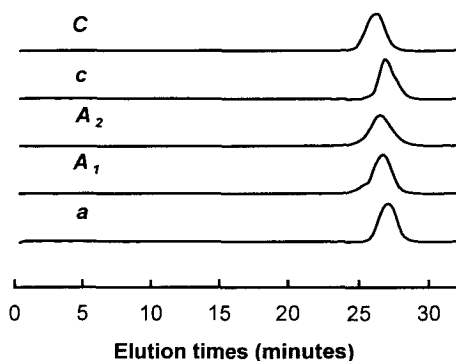


Fig. 2 Gel permeation chromatograms of C_{60} -containing polymethacrylates and the precursor polymers.

Thirdly, the molecular weights of the C_{60} -containing polymers are higher than those of the precursor polymers, indicating that C_{60} has been incorporated into the polymer chain. Except for polymer A_1 , the other C_{60} -containing polymers still have fairly narrow polydispersities. The GPC curves of some C_{60} -containing polymers and their precursor azide polymers are shown in Fig. 2. The T_g of PMMA is significantly increased by the incorporation of C_{60} while that of PnBMA shows only a small increase.

Conclusion

We have shown that allyl-containing poly(alkyl methacrylate)s prepared by group transfer copolymerization can be further functionalized by azide groups to prepare fullerene-containing poly(alkyl methacrylate)s with narrow polydispersities.

C₆₀-containing polymers such as **B**₁ and **B**₂, which possess narrow polydispersities and involving only mono-addition with C₆₀, will be ideal model compounds for the study of the effect of C₆₀ on some solution properties of the parent polymers.

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