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Synthesis, characterization and nonlinear optical properties of copolymers of benzylaminofullerene with methyl methacrylate or ethyl methacrylate

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Abstract

A C_{60} derivative, benzylaminofullerene (BZAF) with a stoichiometry of $[C_{60}H_{1.9}(NHC_6H_5)_{1.9}]$ was synthesized by nucleophilic addition of fullerene with benzylamine in DMSO/*o*-dichlorobenzene. Free radical copolymerization of BZAF with methyl methacrylate or ethyl methacrylate gave high yields of copolymers. The optical limiting threshold of BZAF is comparable with that of C_{60} and stronger than those of the copolymers. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Several methods have been developed to synthesize fullerene-containing polymeric materials since fullerene became available in large quantities [1–8]. Although it has not yet been fully investigated, the free radical copolymerization of fullerene with common monomers may be one of the simplest and most direct methods because fullerene can react with radicals to form various adducts under mild conditions [9–11]. Some efforts have been made on the free radical copolymerization of fullerene with styrene and methyl methacrylate (MMA) [12–14] and the optical properties of copolymer of fullerene with styrene have also been investigated [15]. However, the yields of copolymers are generally low or moderate. The main reason could be that C_{60} contains many double bonds which can easily trap free radicals and terminate the growth of polymer chains.

On the other hand, because of steric hindrance and a decrease in the number of double bonds, fullerene derivatives would have a relatively weaker tendency to trap free radicals. Therefore, these derivatives may give appreciably good yields in free radical copolymerization. It is well known that primary and secondary amines can react with C_{60} to form multi-adducts [16–18]. In the present work, fullerene was allowed to react with benzylamine to produce a multi-adduct benzylaminofullerene (BZAF) $[C_{60}H_n(NHCH_2C_6H_5)_n]$ which was then copolymerized with MMA or ethyl methacrylate (EMA) to give high yields of copolymers.

2. Experimental

2.1. Materials

Fullerene (C_{60}, 99.9%, Peking University) and benzylamine (Merck, Darmstadt, Germany) were used as received. MMA and EMA (both from Fluka, Buchs, Switzerland) were distilled under reduced pressure prior to polymerization. AIBN (Tokyo Chemical Industry, Tokyo, Japan), dimethylsulfoxide (DMSO) (Fisher, Fair Lawn, USA), *o*-dichlorobenzene (DCB) (Aldrich, Milwaukee, USA) and all other reagents were used as received.

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^{-1} using THF as solvent. A calibration line was constructed with polystyrene standards. 90 MHz ^{1}H-nmr spectra were obtained using a Jeol FX90Q spectrometer in $CDCl_3$ with TMS as internal standard. Thermogravimetric analysis (TGA) was made with a TA Instruments 2960 simultaneous DTA–TGA

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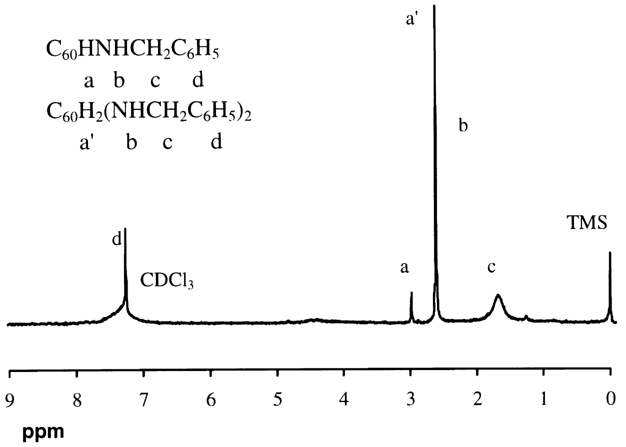

Fig. 1. ^{1}H-nmr spectrum of benzylaminofullerene $[C_{60}H_n(NHCH_2C_6H_5)_n]$ (average $n = 1.9$ in $CDCl_3$ (90 MHz).

under nitrogen at a heating rate of 20°C/min. *FT*ir spectra were recorded on a Perkin–Elmer 1725X *FT*ir spectrophotometer. UV spectra were recorded on a Hewlett Packard 8452A diode array spectrophotometer with a Hewlett Packard Vectra QS/165 computer system. The energy-dependent transmission of all the samples were measured with 7 ns, 532 nm pulses generated from a Q-switched, frequency-doubled Nd:YAG laser. The spatial profiles of the pulses were of almost Gaussian form after passing through a spatial filter. The pulses were then split into two parts: the reflected part was used as a reference and the transmitted part was focused onto the sample by a focusing mirror ($f = 25$ cm). The spot radius of the pulses at the focus was 30 ± 5 mm, measured by conducting Z-scans on the samples. The incident and transmitted energies were monitored by two energy detectors (Laser Precision Rjp-735 probes).

2.2. Preparation of BZAF

Similar to the synthesis of amine-C_{60} adducts [16], benzylamine (223 mg, 2.08 mmol) was added to a magnetically stirred solution of C_{60} (500 mg, 0.69 mmol) in 50 ml of DCB and 10 ml of DMSO. The mixture turned to green and then brown rapidly. Stirring was continued at room temperature for 2 days to allow C_{60} to react completely and a deep brown clear solution was obtained. The solvent was removed by rotary evaporation under reduced pressure. It was then poured into hexane to precipitate the adduct which was further purified by precipitation from THF into hexane three times and dried in vacuo at room temperature for 48 h, to give 630 mg of red brown powder BZAF $[C_{60}H_n(NHCH_2C_6H_5)_n]$. IR (KBr, cm^{-1}): 3420 (-NH-, -OH), 1644, 1425 (C=C), 1182, 734, 689, 575, 525 cm^{-1}. ^{1}H-nmr ($CDCl_3$, δ, ppm): 7.26 (m, $-C_6H_5$), 3.0 (s, $C_{60}H$), 2.6 s, -NH-, $C_{60}H$), 1.6 (m, $-CH_2-$). UV (in chloroform): λmax = 330 nm. The average n value is 1.9 from the weight loss at 600°C in TGA. This is confirmed by comparing the area of signal of $C_{60}H$ ($n = 1$) at 3.0 ppm and that of $C_{60}H$ ($n = 2$) at 2.6 ppm in ^{1}H-nmr spectroscopy (Fig. 1).

2.3. Copolymerization of BZAF with MMA

In a typical procedure, 25 mg of BZAF and 35 mg of AIBN were dissolved in 2 ml of DCB in a polymerization tube. Then 0.5 ml of MMA was added and the solution was stirred for 15 min. The system was deoxygenated and charged with nitrogen alternatively at 0°C for four times. Polymerization was carried out under nitrogen at 60°C for 40 h. The viscous solution was diluted with THF and poured into hexane to precipitate the polymer, which was further purified by the dissolution/precipitation process three times and then dried in vacuo at 60°C for 24 h, to give a brown polymer (yield, 92%).

3. Results and discussion

C_{60} underwent nuclephilic addition readily with benzylamine in DCB/DMSO and the solution turned brown rapidly. No insoluble materials were formed at the end of the reaction. Although C_{60} has a poor solubility in THF, the solubility of BZAF in THF has been improved.

The free radical copolymerization of BZAF with MMA did not give any insoluble materials and the resulting copolymer is soluble in THF, chloroform or toluene. The copolymerization results are shown in Table 1. The yields of BZAF/MMA copolymers are higher than those of C_{60}/MMA copolymers (65–67%) [12]. Thus the derivatization of fullerene does decrease the opportunity for the C_{60} to trap

Table 1
Copolymerization of benzylaminofullerene with methyl methacrylate or ethyl methacrylate

No.	BZAF (mg)	Monomer[a]	AIBN (mg)	Yield[b] (%)	M_w	M_w/M_n	BZAF in copolymer[c] (%)
A	12.5	MMA	20	89	26 200	2.0	2.4
B	25	MMA	35	92	16 400	2.4	5.1
C	12.5	EMA	15	94	47 800	1.8	2.5
D	25	EMA	30	75	23 600	2.0	5.4

[a] 0.5 ml of methyl methacrylate in 2.0 ml DCB at 60°C for 40 h.
[b] Based on the amount of monomer and BZAF used.
[c] From TGA measurements.

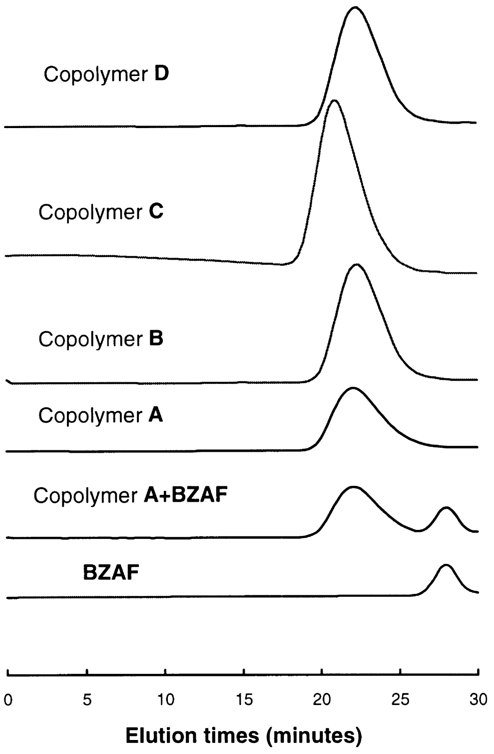

Fig. 2. Gel permeation chromatograms of various samples.

free radicals and thereby terminate the propagation of the polymer chains.

Fig. 2 shows the gel permeation chromatograms of BZAF and its copolymers. BZAF exhibits an elution time at 28 min and the same peak is observed in a mixture of BZAF and copolymer **A**. However, the BZAF peak was not found in all four copolymer samples, showing that BZAF has indeed been copolymerized with MMA or EMA.

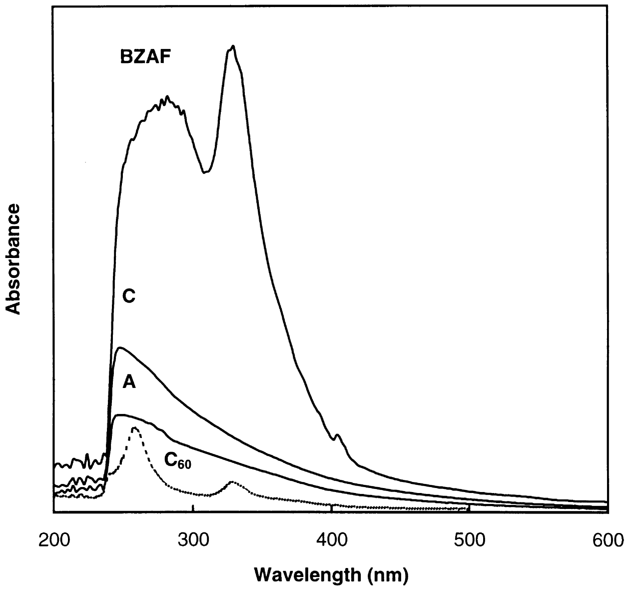

Fig. 3. UV/Vis absorption of C_{60} (0.1 wt%, in chloroform), BZAF (0.5 wt%), copolymer **A** and copolymer **C** (both 5.5 wt%).

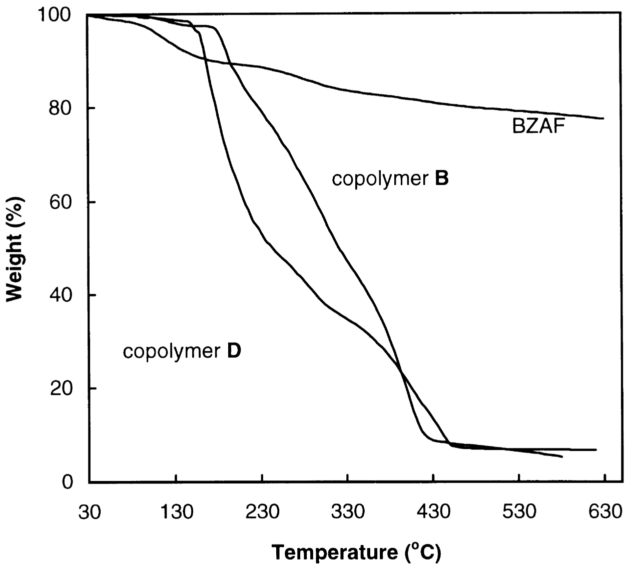

Fig. 4. TGA curves of benzylaminofullerene (BZAF) and its copolymers with methyl methacrylate (copolymer **B**, see Table 1) or ethyl methacrylate (copolymer **D**).

The UV absorption spectra of C_{60} and those of BZAF and BZAF/MMA copolymers in chloroform are shown in Fig. 3. Pure C_{60} shows a main peak at 270 nm and a weak absorption peak at 330 nm, while BZAF shows a main peak at 330 nm and a broad absorption band at approx. 280 nm.

TGA measurements show that BZAF loses the first portion of benzylamino groups between 80 and 150°C and the second portion between 200 and 300°C (Fig. 4). All copolymer samples decompose mainly at 150–450°C but BZAF/MMA copolymer shows a slightly better thermal stability than BZAF/EMA copolymer. The BZAF contents in the copolymers estimated from TGA measurements are in good agreement with the values calculated from the yields by assuming complete incorporation of BZAF in the copolymers.

Copolymer **C** shows a grass transition temperature at 66°C, which is very close to that of 65°C for poly(ethyl methacrylate). Copolymer **D** with a higher BZAF content shows a T_g at 69°C. However, distinct glass transitions could not be detected for copolymers **A** and **B**.

FTIR shows an absorption band of -NH- group at 3450 cm^{-1} in all copolymer samples and both BZAF and

Table 2
Nonlinear optical properties of benzylaminofullerene and various copolymers

Sample	Concentration (mg/ml)	Linear transmittance	Limiting threshold (J/cm^2)
C_{60}	0.1% in toluene	0.68	1.1
BZAF	0.5% in THF	0.82	1.4
A	0.5% in THF	0.95	12
B	0.5% in THF	0.88	12
C	0.5% in THF	0.95	14
D	0.5% in THF	0.88	10

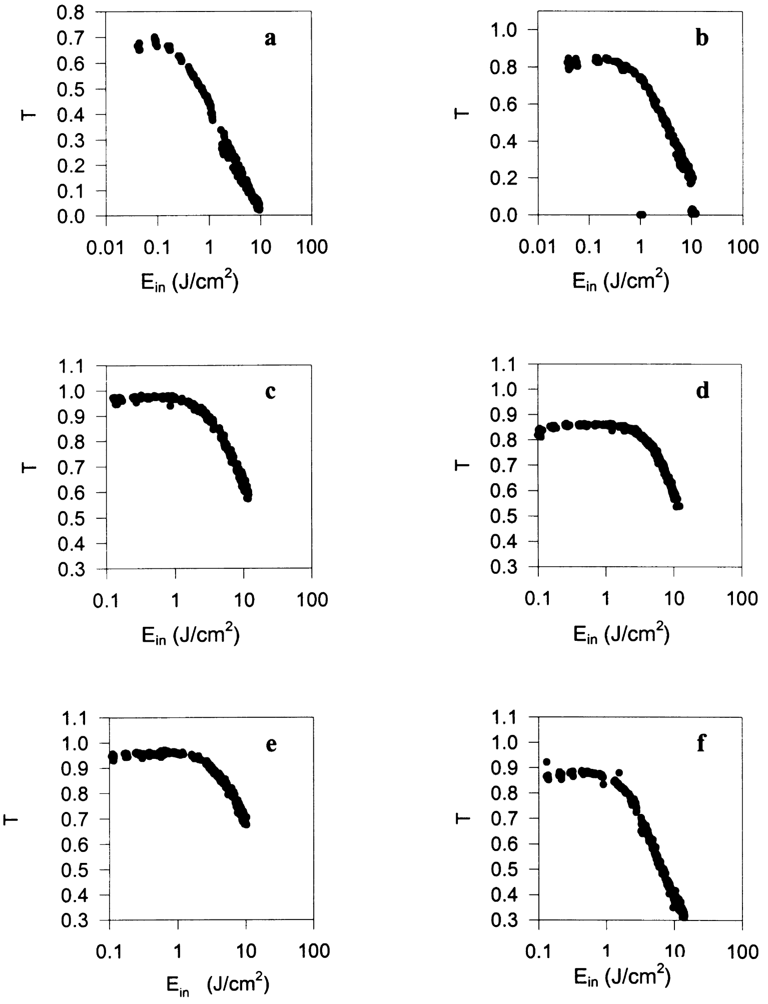

Fig. 5. Optical limiting properties of: (a) C60; (b) BZAF; (c) copolymer **A**; (d) copolymer **B**; (e) copolymer **C**; and (f) copolymer **D**.

copolymers show the typical absorption of C_{60} at 1182 cm^{-1}.

Benzylaminofullerene and all its copolymers do show nonlinear optical effects as C_{60}. Fig. 5 displays the optical limiting behaviour in the energy-dependent transmission of C_{60}, BZAF and the four copolymers. The limited threshold is defined as the input fluence at which transmittance falls to 50% of the linear transmittance. Table 2 summarizes all the measured limited thresholds. It is clear that the performance of BZAF is comparable with that of C_{60} and those of the copolymers are weaker by one order of magnitude in terms of their limiting threshold values.

4. Conclusions

BZAF was prepared by the addition of C_{60} with benzylamine in DCB/DMSO. BZAF containing an average 1.9 benzylamino groups can copolymerize with MMA or EMA initiated by AIBN. No cross-linking occurs in the free radical copolymerization and BZAF is completely incorporated into the polymer chains. These BZAF-containing polymethacrylates still show nonlinear optical properties.

Acknowledgements

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