Polymerization of Ethyl Acrylate Using Hyperbranched Polyglycerol with Multi-RAFT Groups as Chain Transfer Agent

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ABSTRACT: Surfacing hydroxyl groups of hyperbranched polyglycerol (PG) were transformed into trithiocarbonates (TTC), an efficient multi radical addition-fragmentation transfer (RAFT) agent, to mediate the polymerization of ethyl acrylate (EA) under controllable conditions, and PG with multiarm PEA was obtained. In this system, PG was a part of Z groups, and trithiolcarbonates were bonded directly to the PG, whereas the growing PEA macroradical was detached. The molecular weight and the molecular weight distribution of the products were in the range of 1.05–3.24 $\times$ 10^4 g/mol and 1.28–1.42, respectively, when the concentration ratio of EA to PG-TTC was 39.8. The number of the PEA arms was about 16. It was found that the measured molecular weights of the products were deviated from the theoretical value, and the molecular weight distribution was broadened with the conversion due to the termination between the leaving macroradicals. The final and the intermediate products were characterized by NMR in detail. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2203–2209, 2006

Key words: hyperbranched; grafter copolymers; molecular weight distribution; polyglycerol; radical addition-fragmentation transfer

INTRODUCTION

Multiarm polymers have evoked much interest because of their topology, for example, lower bulk and solution viscosities than their linear counterparts with the same molecular weight.[1–3] Though synthesis of star polymer was described early in 1948,[4] the convenient synthesis of well-defined multiarm polymer was a challenge until the advent of living polymerization techniques.[5,6] Although anionic polymerization was once the main route to synthesize multiarm polymer, it was generally indirect, limited, or tedious.[7]

Recently, dendrimer and hyperbranched polymer with dense surfacing groups have been widely developed as useful scaffolds for modification of polymers with complex topology, and simple chemical modification of such molecules can lead to molecular capsule and compartment for guest molecules or particles. Dendrimers, a well core-shell structured polymer, have been successfully used as template for quantum-confined metal or semiconductor nanoparticles or as carrier of catalyst,[8–10] but the limitation was originated from their tedious preparation and limited growth. In contrast, hyperbranched polymers are conveniently prepared on large scales in one-pot procedures via polymerization of ABm-type monomers, and still possess the most characteristics of dendrimer: dense surfacing groups and interior voids. Anionic polymerization of glycidol now can be well controlled, thus conveniently leads to hyperbranched polyglycerol (PG) with controlled molecular weight and narrow polydisperity ($1.2 < M_w/M_n < 1.5$).[11] PG has hydroxyl groups distribution from core through surface, and those on surface make up to 60% of the total hydroxyl functionalities.[11] The densely populated peripheral hydroxyls of PG constitute a platform of a variety of chemical modifications. To prepare copolymers with multiarms using PG as core molecules in the mild conditions, the radical addition-fragmentation transfer (RAFT) technique was used. There were limited examples which used superbranched polymer to prepare the multiarm copolymer via RAFT techniques. Jesberger et al.[12] reported the successful synthesis of a multiarms copolymer, using superbranched polyester as core, by multifunctional reversible addition-fragmentation chain transfer agents.

As it is well known, there are two ways to prepare the star or comb polymers by RAFT techniques. In the first method, the core or backbone acts as a part of the leaving group (R group), and the generated radicals can either grow, transferred to another RAFT agent, or terminate with a second radical, and so, the molecular weight distribution was broadened.[13,14] In the other method, the core or backbone acts as a part of Z group,

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and the RAFT groups are always bonded directly on the core/backbone, whereas the growing macroradical was attached.[15,16] In this method, a well-defined polymer with narrow molecular weight distribution was obtained. However, the RAFT process may be more and more difficult; especially, the arms with high molecular weight were formed because of the shielding effect of the polymer arms. Here, we report the synthesis of a multiarm polyethyl acryalte on PG core as a part of Z group.

EXPERIMENTAL

Materials

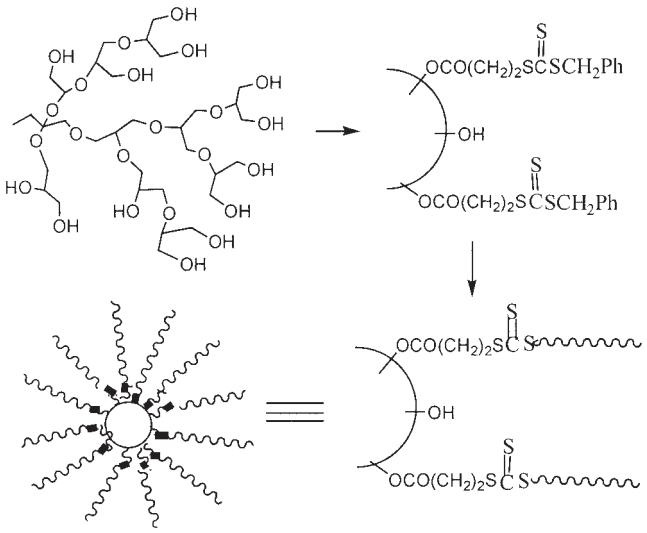
2,2′-Azobis(2-methyl-propionnitrile) (97%) (AIBN), 1,1,1-Tris(hydroxymethyl)propane (TMP), dioxane, carbon disulfide, triethylamine, chloroform, benzyl bromide, toluene, *p*-toluenesulfonic acid, 3-mercaptopropanic acid, and sodium borohydride were used directly; *N*,*N*-dimethylformide (DMF) and glycidol were dried by calcium hydride and then distilled; ethyl acrylate (99%) (EA) was distilled under reduced pressure, just before use. All chemicals were purchased from Aldrich or Acros. Benzoylated dialysis tubing (D-7884, MWCO 1200) was purchased from Sigma.

Preparation of PG[11]

Polymerization was carried out in a reactor equipped with a mechanical stirrer and dosing pump under argon atmosphere. 1,1,1-Tris(hydroxymethyl)propane (TMP, Fluka) 2.78 g (10%) was deprotonated with 0.7 mL of potassium methylate solution (3.7*M* in methanol, Fluka) by distilling off excess methanol from the melt. A 50-g aliquot of glycidol was slowly added at 95°C over 12 h. The product was dissolved in methanol and neutralized by filtration over cation-exchange resin. The polymer was twice precipitated from methanol solution into acetone and subsequently dried for 15 h at 80°C *in vacuo*. Polyglycerol (42.7 g) was obtained as a transparent, highly viscous liquid, with the yield of 80%. [M_n = 2000 (VPO), M_w/M_n = 1.4 (GPC), average 26 hydroxyls each molecule*].

Preparation of PG with thiol groups

Dried polyglycerol with M_n = 2000 (5 g, 67 mmol OH) and 3-mercaptopropanic acid (5.75 g, 54 mmol) were charged in a three-necked round-bottom flask. An azeotrope was arranged using molecular sieves and dropping funnel. The polyglycerol was slowly dissolved in the acid, and then 5 mL of toluene was added. The reaction was heated to 70°C and followed by the addition of 50 mg of catalyst, *p*-toluenesulfonic acid; the temperature was then raised to 140°C and was continued for 16 h. The polymer was precipitated in cold methanol. Further purification of the polymer was carried out by repeated precipitation, with the yield of 85%.



Scheme 1 Outline of the synthesis of multiarm polyethyl acrylate.

Preparation of PG with trithiocarbonate groups

Triethylamine (6.06 g, 60 mmol) in $CHCl_3$ (20 mL) was added to a stirred solution of the above thiol functionalized PG derivative (5.94 g, 30 mmol SH) and carbon disulfide (4.56 g, 60 mmol) in $CHCl_3$ (20 mL) at room temperature. The solution was allowed to mix for 1 h, before benzyl bromide (5.64 g, 33 mmol) was added. The mixture was stirred for 2 h, poured into a cold solution of aqueous 10% HCl, and the organic layer was separated as a thick yellow oil. The product PG with trithiocarbonate groups (PG-TTC) was purified by dialysis against chloroform for 8 h, with the yield of 94%.

Synthesis of PG with poly(ethyl acrylate) arms

A typical operation was as follows: 1.06 g of PG-TTC (2.66 mmol trithiocarbonate), 10.64 g of ethyl acrylate (106 mmol), and 16 mg of AIBN (0.0975 mmol) were mixed, and bubbled with nitrogen for 0.5 h, then heated with stirring at 80°C for 5–25 h. The polymer was recovered by precipitation from petroleum ether and purified by repeated dissolution/precipitation from chloroform/petroleum ether.

*It is easy to understand that one monomer unit in the polyglycerol corresponds to one OH, regardless of branched polymerization or linear polymerization, because two hydroxyl groups of glycidol were reacted.[17–19] In this case, the number of OH is nearly equal to the polymerization degree of polymer, that is 2000/74 = 27 (74 is the difference of 94 (mass of glycidol) and 18 (mass of water). Considering the three hydroxyl groups of the core molecule, 1,1,1-Tris(hydroxymethyl) propane was reacted, so that the number of hydroxyl groups should be 27 − 1 = 26.

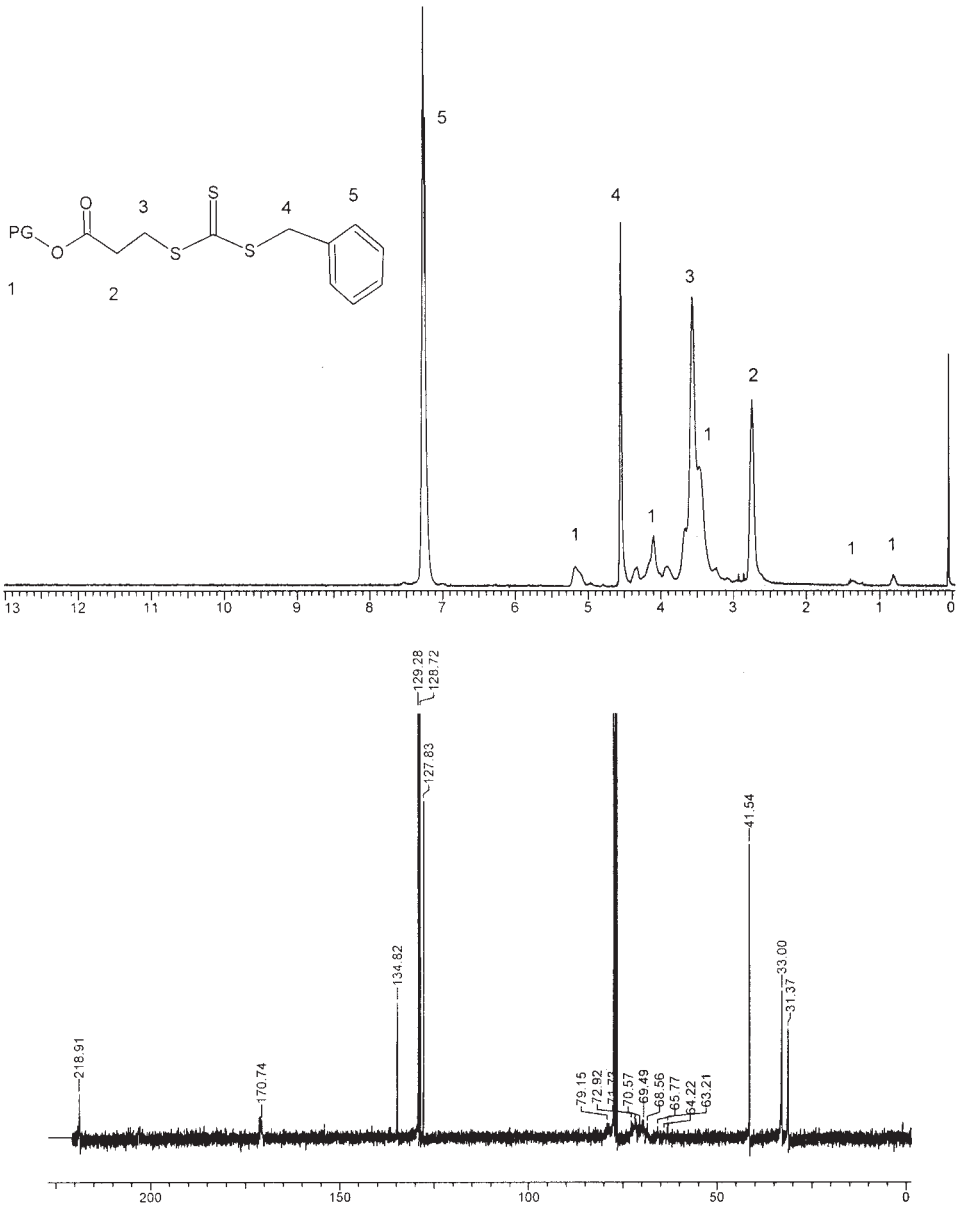


Figure 1 ^{1}H-NMR and ^{13}C-NMR of multi-RAFT derivative of PG in $CDCl_3$.

Cleavage of poly(ethyl acrylate) arms from PG

A typical operation was as follows: to a solution of 0.5 g of the above product in 15 mL chloroform, 0.25 g of triethylamine was added and stirred for 24 h at 60°C, then absolute formic acid was added to adjust the pH to 6 and stirred for another 24 h. The solution was distilled to viscous liquid, and then extracted with acetone three times. The extracted solution was concentrated to 1/3 of its original volume, and then precipitated with cold methanol. After separation, the blocked PEA was obtained.

Measurement

^{1}H-NMR and ^{13}C-NMR were recorded on Bruker AMX 300. Gel permeation chromatography (GPC) was performed using chloroform as eluent at a flow rate of 1.0 mL/min at room temperature; injection volume: 100–150 μL; column set: 5 μm PSS SDV gel, 10^4, 10^3, 10^2Å, 30 cm each; detectors: TSP differential refractometer and TSP UV detector operated at 254 nm. PS standards were used for the calibration of the column set. Vapor pressure osmometry was carried out using a Knauer Vapor Osmometer at 35°C with chloroform in a concentration range of 5–10 mg/mL, and benzyl (Merck) was used for calibration.

RESULTS AND DISCUSSION

Derivatization of hydroxyl of PG

The conversion of hydroxyl groups of PG to thiol and then trithiocarbonate could be described as given in Scheme 1.

TABLE I
Molecular Weight and Polydisperity Data for Poly(ethyl acrylate) Mediated by PG-TTC[a]

[EA][a]/[PG-TTC]	Conversion of BA (%)	M_n (10^{-4} g/mol)					M_w/M_n	
		Theor.[b]	GPC	NMR[c]	Broken[d]	Calcd.[e]	PG-PEA	PEA
39.8	10	1.27	1.00	1.05	0.04*	1.27	1.28	
	15	1.59	1.30	1.40	0.05*	1.43	1.32	
	21	1.97	1.80	1.64	0.07*	1.75	1.36	
	27	2.35	2.14	2.01	0.08*	1.91	1.36	
	39	3.12	2.52	2.38	0.10**	2.23	1.39	1.21
	68	4.96	3.49	3.24	0.18**	3.51	1.42	1.20
28.4	11	1.13	1.01	1.10	0.02*	0.95	1.25	
	14	1.27	1.16	1.30	0.03*	1.11	1.24	
	23	1.68	1.43	1.39	0.06*	1.59	1.27	
	31	2.04	1.76	1.58	0.07*	1.75	1.31	
	43	2.59	2.02	2.49	0.08*	1.91	1.33	
	65	3.59	2.28	2.55	0.12**	2.55	1.35	1.19

[a] Polymerization conditions were as shown under Experimental.
[b] Theoretical values were calculated from conversion and the concentration of trithiolcarbonates of PG.
[c] By comparison of the integration area of ^{1}H-NMR peak corresponding to phenyl end group and methylene of poly(ethyl acrylate), respectively.
[d] Object product was cleaved by reduction with sodium borohydride, and then, the cleaved PEA was measured by GPC.
[e] Calculated molecular weight of object product = $MW_{\text{blocked}} \times 16 + 2000$ (MW of PG) $- 16$ (hydrogen atom number of reacted hydroxyls of PG) + 271 (mass of trithilcarbonate) $\times$ 16 (atm number).
* The values were obtained by VPO.
** The values were obtained by GPC.

6The PG with thiol groups was characterized by ^{1}H-NMR, and the assignment of the peaks is the same as described in literature[11]: 0.79 (t, C*H*$_3$CH$_2$ of TMP, the core of PG), 1.25 (CH$_3$C*H*$_2$ of TMP), 1.63 (s, SH), 2.59 (t, OCOC*H*$_2$CH$_2$), 2.68 (t, CH$_2$C*H*$_2$SH), 3.0–3.6 (m, PG), 4.07 (CH$_2$ of PG attached to OCO), 5.15 ppm (CH of PG attached to OCO). According to the peak area ratio of PG core at 3.0–3.6 ppm to SH at 1.63 ppm, about 65% of hydroxyl was modified, in other words, there were an average of 17 thiol groups on each PG molecule. Figure 1 shows the ^{1}H- and ^{13}C-NMR of PG with trithiocarbonate groups; the assignment of its peaks is as follows: δ (ppm): 0.79 (t, C*H*$_3$CH$_2$ of TMP, the core of PG), 1.25 (CH$_3$C*H*$_2$ of TMP), 2.59 (t, OCOC*H*$_2$CH$_2$), 2.75 (br, C*H*$_2$—S—), 3.0–3.6 (m, PG), 4.07 (CH$_2$ of PG attached to OCO), 4.56 (s, C*H*$_2$Ph), 5.15 (CH of PG attached to OCO), 7.24 (br, Ph). ^{13}C-NMR ($CDCl_3$) δ (ppm): 31.37 (t, CH$_2$—S—), 33.00 (CH$_2$—C═O), 41.54 (CH$_2$Ph), 127.83, 128.72, 129.28, 134.82 (Ph), 170.74 (—C═O), 218.91 (C═S), and 63.21, 64.22, 65.77, 68.56, 69.49, 70.57, 71.72, 72.92, 79.15 ppm for PG. According to the peak area ratio of PG core at 3.0–3.6 ppm to trithiocarbonate at 4.56 ppm, or SH at 1.63 ppm to trithiocarbonate at 4.56 ppm, 90% SH of PG was converted to trithiocarbonate, which means there were 16 trithiocarbonate groups per PG molecule.

Polymerization of EA in the presence of PG-TTC

The data of bulk polymerization of ethyl acrylate (EA) mediated by PG-TTC are listed in Table I, in which, in

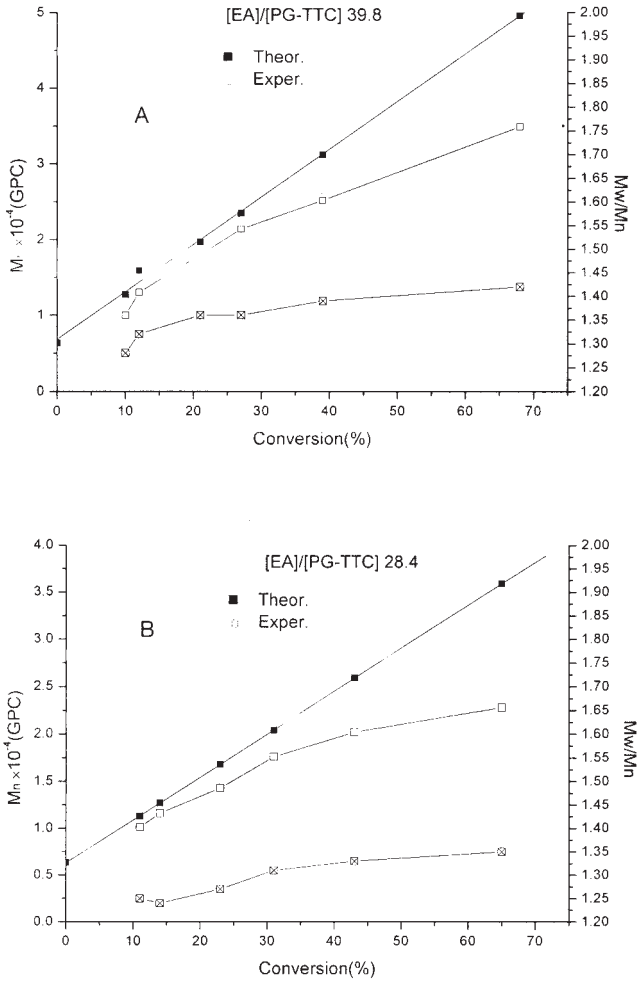


Figure 2 The relationship of M_n and M_w/M_n with conversion in different ratios of [EA]/[PG-TTC] (A: 39.8; B:28.4).

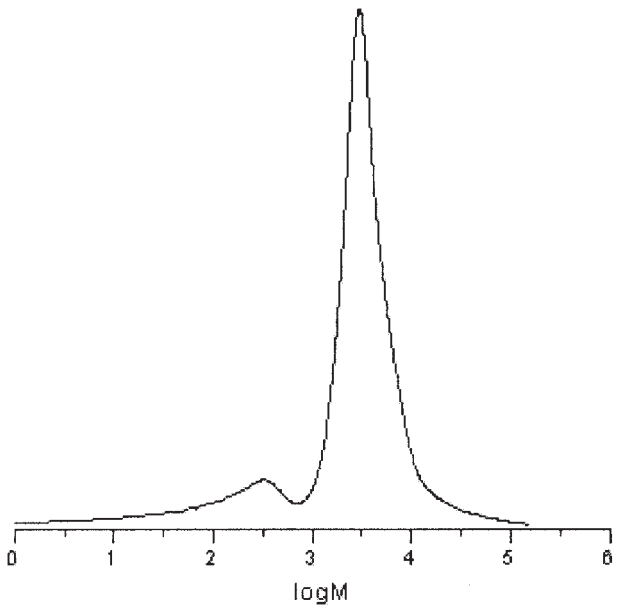


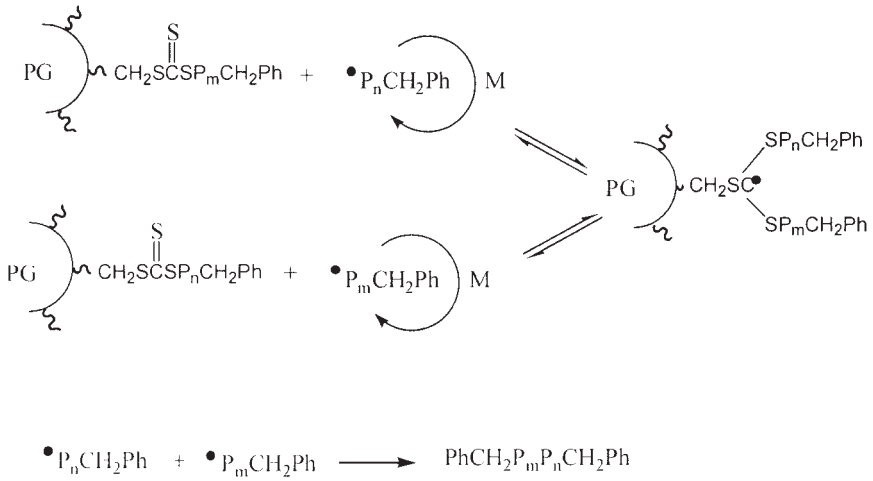
Figure 3 GPC trace of PG-PEA (conversion: 68%).

all cases, the molecular weight was dependent on the conversion of the monomer, and the molecular weight distribution was generally less than 1.5, which means the polymerization of EA in the presence of PG-TTC was controllable. Figure 2 shows the relationship of molecular weight and molecular weight distribution with conversion in different concentrations of PG-TTC. The theoretical molecular weight of the object products could be derived from the following equation:

$$MW_{\text{theor}} = [\text{EA}]/[\text{PG-TTC}] \times M_{\text{EA}} \times \text{conversion} + M_{\text{PG-TTC}}$$

where MW_{theor} is the molecular weight of object product, [EA] and [PG-TTC] are the initial concentrations of EA and PG-TTC, and M_{EA} and $M_{\text{PG-TTC}}$ are the molecular weight of EA and PG-TTC, respectively. It was observed that, in all cases, the molecular weight of object product was deviated from the theoretical values, and the more the conversion, the greater the deviation. The explanation of this phenomenon was involved in calibrating GPC with linear polystyrene standards, when the measurement of PG with multiarms PEA was performed. However, the molecular weight distribution was narrow in the low conversion, and as the conversion increased, the molecular weight distribution was broadened. In our cases, as we mentioned before, the trithiocarbonates were bonded on the PG core, and the macroradicals formed by the reinitiation of the leaving benzyl group can either transfer to the PG-TTC or terminate with other macroradicals. In the low conversion, the transfer is easy to conduct, and the termination could be negligible. As the conversion increased, the trithiolcarbonate groups bonded on PG core may be enveloped because of the entanglement of the increased polymer chains, and the access of the macroradicals to the transfer sites of PG-TTC was impeded.[14] In this case, the termination probability between the macromolecules was increased, so that the molecular weight distribution was widened. In the similar conditions, as Table I and Figure 2 indicate, high concentration of PG-TTC would lead to the products with low molecular weight, but its effect on molecular weight distribution was limited.

Figure 3 is the typical GPC diagram of the object product (conversion: 68%); it was noticed that, besides the main product peak, there always appeared a small peak with low molecular weight for the samples in which the conversion was higher than 27%, and this is the linear PEA. In the whole polymerization process, the trithiocarbontes were bonded on the PG core, which is a part of Z group; thus, it is impossible to form the core radical. Furthermore, if the termination



Scheme 2 Schematic formation mechanism of multiarm star polymer and linear byproducts.

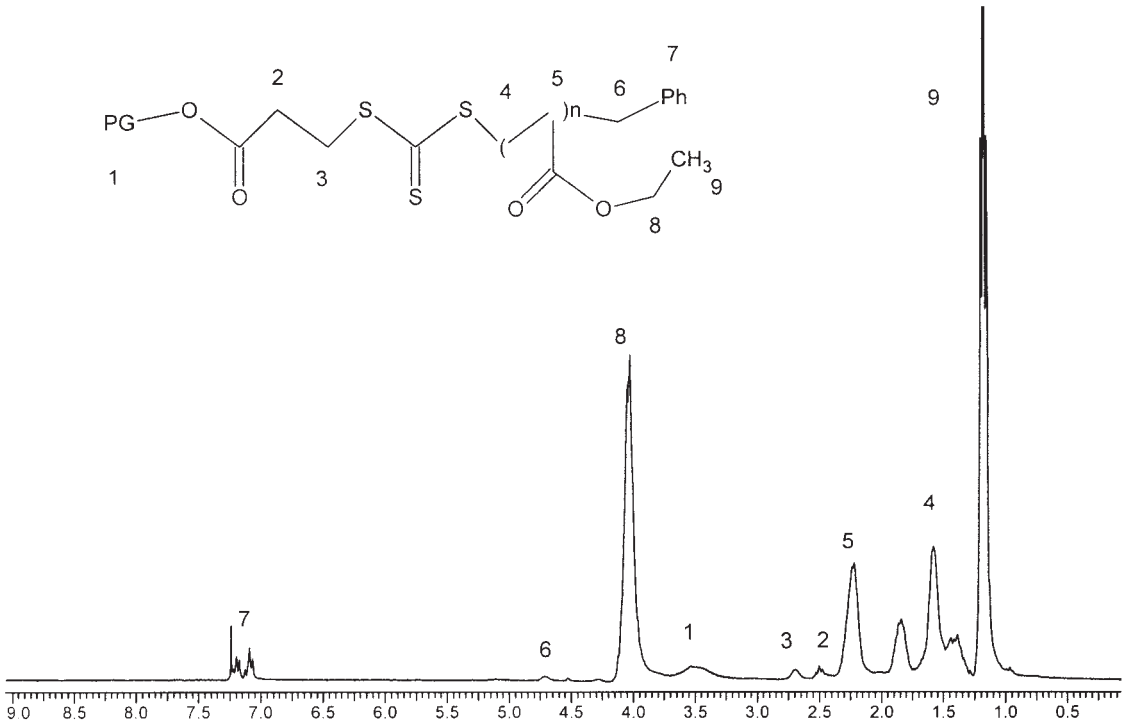


Figure 4 ^{1}H-NMR of PG with multiarms PEA in $CDCl_3$.

was carried out between the core radicals, then the molecular weight of the terminated product should be greater than the object product, but Figure 3 indicates that only the polymer with low molecular weight was observed. Therefore it could be reliably concluded that this small peak should be attributed to the termination of the leaving macroradicals, as Scheme 2 shows.

Determination of the number of PEA arms

To determine the efficiency of PG-TTC, the PEA was cleaved from the PG, in the presence of $NaBH_4$; and the molecular weight of PEA was then measured by VPO and GPC. We found that, in the low conversion, the experimental values were approachable to the theoretical values, which means, in our system, nearly all of trithiocarbonates took part in the polymerization, and the number of the arms was about 16. However, the deviation was serious as the conversion increased; the termination between macroradicals is the main cause.

Figure 4 provides a clear information on the structure of the copolymerization product of EA, mediated by PG-TTC, in which all the signals such as 1.0–1.25 (—CH_3 of —OC_2H_5), 4.1 (—CH_2— of —OC_2H_5), 1.6 (—CH_2— of —CH_2CHCOO—), and 2.25 ppm (—CH— of —CH_2CHCOO—) for poly(EA), and 2.5 (—CH_2 connected with carboxyl), 2.7 (—CH_2— connected with trithiolcarbamate), 3.20–3.75 (PG), 7–7.25 ppm (phenyl) for PG-TTC appeared. Owing to the high contents of the end groups of benzyls, the average polymerization degree of EA or the molecular weight based on this degree could also be derived from the NMR, using the following formula:

$$M_n = \frac{5A_{\mathrm{CH_2EA}}}{2A_{\mathrm{PEN}}} \times M_{\mathrm{EA}}.$$

Here, A_{CH2EA} is the proton peak area of methylene of poly(ethyl acrylate) at 4.1 ppm, A_{PEN} is the proton peak area of phenyl at 7–7.25 ppm, and M_{EA} is the mass of EA. The values of NMR and GPC in Table I are close in the low conversion of EA; but huge deviation was found for the samples with high conversion, because of the different hydrodynamic volume of the PG of multiarms with high molecular weight and linear polystyrene standard.

CONCLUSIONS

Polyglycerol with multiarms of polyethyl acrylate was successfully synthesized by RAFT technique. In this system, the trithiolcarbonate was always bonded on the polyglycerol core molecule, whereas the growing PEA macroradical was detached. As the conversion increased, RAFT process was more difficult to be carried out because of the entanglement of PEA with high molecular weight, and the termination between the leaving macroradicals was detected.

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