Synthesis of Amphiphilic Graftcopolymers from Polystyrene Macromonomer

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ABSTRACT: Graftcopolymers of well-defined structure and composition were prepared by the radical copolymerization of polystyrene macromonomers with functional comonomers. The macromonomer was prepared by the polymerization of styrene in the presence of monoiodoacetic acid as a chain transfer agent, followed by an end-capping reaction with glycidyl methacrylate. In the case of 2-hydroxyethyl methacrylate as a comonomer, hydrophilic graftcopolymer soluble in polar solvent was obtained and characterized by thin layer chromatography. In the case of perfluoroalkyl acrylate as a comonomer, hydrophobic graftcopolymer soluble in ordinary solvent was obtained.
    KEY WORDS   Graftcopolymer / Macromonomer / Styrene / Hydroxyethyl Methacrylate / Fluoroacrylate /

Recently, the synthesis of tailored graftcopolymers by the macromonomer technique has been of interest in connection with the ease of the combination of a wide variety of monomers. The macromonomer technique consists of the introduction of branches by the copolymerization of the preformed macromonomers with various comonomers to obtain well-defined graftcopolymers; the number and length of branches in the backbone polymer can be controlled.[1,2] We have already reported on the syntheses and characterization of methyl methacrylate–stearyl methacrylate graftcopolymers.[3] This paper reports on the synthesis of amphiphilic graftcopolymers from polystyrene macromonomer prepared by free radical polymerization using a chain transfer agent. As functional comonomers, 2-hydroxyethyl methacrylate and perfluoroalkyl acrylate was used to obtain hydrophilic and hydrophobic graftcopolymers, respectively. The method of preparation is shown in Scheme I.

EXPERIMENTAL

Materials

Styrene (St), methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA) and glycidyl methacrylate (GMA) were purified by vacuum distillation. Azobisisobutyronitrile (AIBN) and hydroquinone were recrystallized from methanol. All solvents were dried and distilled before use. Monoiodoacetic acid and lauryldimethylamine were used as received. Perfluoroalkyl acrylate (FA) was kindly provided by Asahi Glass Co. and distilled before use. The perfluoroalkyl acrylate is a commercial mixture of
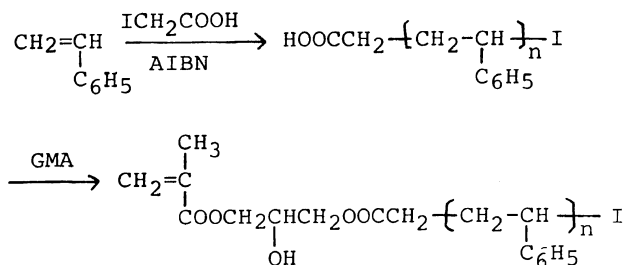
$$CH_2 = CHCOOCH_2CH_2C_nF_{2n+1},$$

with the average number n equal to 8.82.
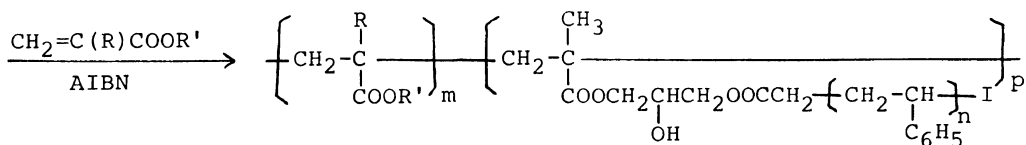
Prepolymers

St, AIBN, and monoiodoacetic acid were weighed into an ampule and degassed and sealed under vacuum. Polymerization was carried out in bulk at 60°C to an appropriate conversion. The polymer

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Scheme I

$$CH_2=CH \atop C_6H_5 \xrightarrow[\text{AIBN}]{ICH_2COOH} HOOCCH_2 \left(CH_2-CH \atop C_6H_5\right)_n I$$

$$\xrightarrow{GMA} CH_2=C \atop COOCH_2CHCH_2OOCCH_2\left(CH_2-CH\right)_n I \atop \quad OH \qquad\qquad C_6H_5$$

copolymerization with

$$\xrightarrow[\text{AIBN}]{CH_2=C(R)COOR'} \left\{CH_2-C \atop COOR'\right\}_m \left\{CH_2-C \atop COOCH_2CHCH_2OOCCH_2\left(CH_2-CH\right)_n I \atop \quad OH \qquad\qquad C_6H_5\right\}_p$$

1 R=CH₃, R'=CH₂CH₂OH

2 R=H,   R'=CH₂CH₂CₙF₂ₙ₊₁   ($\bar{n}=8.82$)

was precipitated into methanol, purified three times by reprecipitation from benzene into methanol and dried under vacuum. The carboxyl group content was determined by titrating the polymer in dimethylformamide (DMF) with 0.1 N potassium hydroxide aqueous solution, using thymol blue as an indicator. The agreement of M_n observed by VPO in benzene with that calculated by titration confirmed the purity of the carboxylic terminated prepolymer. GPC measurement in tetrahydrofuran (THF) was used to check the molecular weight distribution.

Macromonomers

The carboxylic terminated prepolymer was reacted with glycidyl methacrylate (50 mol% excess) at 140°C in xylene with small amounts of hydroquinone and lauryldimethylamine to prepare the macromonomer having a methacryl group at one end. The reaction was carried out in an ampule under nitrogen to prevent coloration. The polymer was precipitated into methanol, purified three times by reprecipitation from benzene into methanol and dried under vacuum. It was characterized by VPO and GPC measurement.

Graftcopolymers

The St macromonomer thus obtained was copolymerized in an ampule with various comonomers to complete the conversion to various graftcopolymers using AIBN for several days in a homogeneous solution. In the case of HEMA as a comonomer, DMF was chosen as the solvent and the graftcopolymer was precipitated into diethyl ether. In the case of FA as a comonomer, benzotrifluoride was chosen as the solvent and the graftcopolymer was precipitated into cyclohexane. The graftcopolymer was characterized by elemental analysis and GPC.

Characterization of the St–HEMA graftcopolymer was carried out by the following procedure. The PSt content was analyzed by UV spectrometry in the DMF or THF solvent, using the calibration curve for PSt. Soxhlet extraction of the graftcopolymer was carried out for 6 hours, first with cyclohexane to remove homopoly-St and then with methanol to remove homopoly-HEMA. In the case of MMA-rich ternary graftcopolymers consisting of St–(HEMA-*co*-MMA), acetonitrile was used in place of methanol. Thin layer chromatog-

raphy was carried out with a silica gel plate (Eastman Kodak 1381) and fluorescent indicator (No. 6060). THF was used as a spotting solvent and either methanol or ethyl acetate was used as the developing solvent.

RESULTS AND DISCUSSION

Synthesis of Macromonomer

St macromonomer can be obtained by endcapping the polystyrene living anion with methacryloyl chloride.[2] In the present work, free radical polymerization was adopted as a practical procedure for preparing prepolymers. Various chain transfer agents were compared in synthesizing carboxylic-terminated St prepolymers. Thioglycolic acid and tribromoacetic acid were found to be too reactive in the chain transfer reaction. The reported values for the chain transfer constants C_s are 14 and 3, respectively.[4] It was found that carboxylic-terminated PSt could be obtained at a low conversion by a chain transfer reaction, but an increase in mo-

lecular weight was observed at a higher conversion due to consumption of the chain transfer agent, resulting in the presence of impure materials. When monoiodoacetic acid as a chain transfer agent was used, a carboxylic-terminated prepolymer of molecular weight range 2000—8000 was easily obtained at moderate conversion as expected from its C_s value of 0.8.[4] Table I gives the results of the preparation of several prepolymers which were characterized by molecular weight determination with GPC, VPO, and end group titration. The approximate chain transfer constant C_s was calculated to be from 0.41—0.51, using the integrated Mayo equation for the high conversion system.

The terminal carboxyl group of St prepolymer was reacted with glycidyl methacrylate at 140°C in xylene in the presence of hydroquinone and lauryldimethylamine. After 4 h, the reaction proceeded nearly 90% and the macromonomer was characterized by VPO and GPC. It was difficult for the purity of the macromonomer to exceed 90% especially when the conversion was high in the prep-

Table I. Synthesis of St prepolymer[a]

No.	$\dfrac{[S]_0{}^b}{[M]_0}$	AIBN mol%	Time h	Conversion wt%	M_n Tit.[c]	M_n VPO	$C_s{}^d$
31	0.0609	0.2	7.0	22.4	3300	4000	0.52
32	0.0617	0.2	7.5	24.7	3500	3800	0.47
34	0.0637	0.4	5.7	25.1	3200	3300	0.51
36	0.0281	0.4	3.0	17.1	6080	7660	0.61
38	0.0535	0.4	4.5	19.1	4670	4300	0.41

[a] Bulk, 60°C.
[b] Molar feed ratio of monoiodoacetic acid to monomer.
[c] M_n by carboxyl end group titration assuming one COOH per molecule.
[d] Chain transfer constant calculated from $C_s = \log\ (1 - \alpha[M]_0/n[S]_0)/\log\ (1 - \alpha)$: α, conversion; n, degree of polymerization by titration.

Table II. Synthesis of St macromonomer[a]

No.	M_n of PSt VPO	Time h	Yield wt%	Unreacted PSt[b] wt%	M_n of macromonomer VPO
332	3800	5	90.4	10.0	5200
341	3300	4	89.9	27.0	4300
361	7660	4	94.6	7.0	7690
381	4300	4	94.6	5.0	4900

[a] In xylene, 140°C.
[b] By titration of COOH group.

aration of the prepolymer. The results are shown in Table II.

Preparation of Graftcopolymer

The St macromonomer thus obtained was co-polymerized using AIBN with hydrophilic or hydrophobic comonomers to complete conversions so as to obtain amphiphilic graftcopolymers at 60°C for several days in a homogeneous solution. In the case of HEMA as a hydrophilic comonomer, DMF was used as the solvent, since gelation was observed in THF. In Table III is shown binary graftcopolymerization and in Table IV, ternary graftcopolymerization. The graftcopolymer was soluble in various organic solvents, indicating the amphiphilic nature of the graftcopolymer. The contaminated St prepolymer and unreacted macromonomer were removed by reprecipitation from dimethylformamide, and placed in diethyl ether. The St content in the graftcopolymer was obtained from elemental analysis and UV spectrometry. The experimental results show a decrease in St content in the graftcopolymer compared with the

initial feed ratios. To explain this, the reactivity of St macromonomer was studied. Figure 1 shows the copolymer composition curve of St macromonomer (M_2) and HEMA (M_1). The copolymerization was terminated at low conversion and the
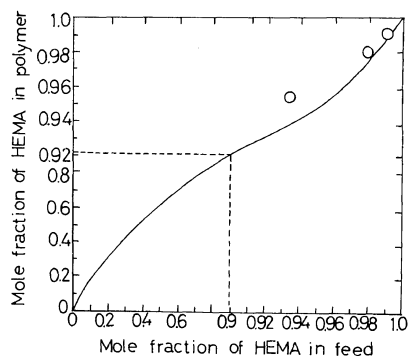

Figure 1. Copolymer composition curve for St macromonomer (M_2) and HEMA (M_1): ◯, copolymerization in DMF at 60°C with AIBN; —, Calculated by $r_1 = 1.0$, $r_2 = 0.29$ for HEMA (M_1)–MMA (M_2), bulk at 60°C with BPO.

Table III. Preparation of St–HEMA graftcopolymers[a]

No.	PSt in feed			Graftcopolymer			
	M_n VPO	wt%	mol%	Yield wt%	M_n GPC	PSt wt% from	
						C%	UV
3412	4300	68.7	6.2	69.0	14000	46.2	—
3611	7690	23.9	0.7	79.2	—	11.2	18.7
3612	7690	47.9	1.5	81.8	16000	34.3	38.9

[a] 60°C in DMF, AIBN 0.2 mol%, 7 days.

Table IV. Preparation of St–(HEMA-*co*-MMA) graftcopolymers[a]

No.	Feed					Graftcopolymer				
	M_n, PSt VPO	wt%		mol%		Yield wt%	M_n GPC	C%		PSt wt%, UV
		PSt	HEMA	PSt	HEMA			obs.	calcd.[b]	
3414	4300	20.0	39.9	0.65	43.0	91.4	44300	69.6	64.6	21.7
3415	4300	18.2	53.0	0.64	58.9	85.3	25300	60.6	63.5	12.7
3614	7690	23.1	39.0	0.44	43.5	84.1	40900	63.1	65.6	16.7
3615	7690	24.0	51.6	0.48	61.6	87.7	37500	61.6	65.3	15.7

[a] 60°C in DMF, AIBN 0.2 mol%, 7 days.
[b] Assuming a composition the same as that of the feed.

Table V. Fractionation of graftcopolymers[a] (Soxhlet extraction)

St–HEMA graftcopolymer

No.	PSt wt%[b]	MeOH insoluble part		MeOH soluble part	
		wt%	PSt wt%[b]	wt%	IR
3611	18.7	62.6	22.7	37.4	PHEMA
3612	38.9	91.0	37.9	9.0	PHEMA

St–(HEMA-co-MMA) graftcopolymer

No.	PSt wt%[b]	MeOH insoluble part		MeOH soluble part	
		wt%	PSt wt%[b]	wt%	IR
3415	12.7	74.1	13.6	25.9	Graft
3615	15.7	71.0	18.3	29.0	Graft

[a] Insoluble in cyclohexane.

[b] Determined by UV.

copolymer was precipitated in diethyl ether to remove the unreacted macromonomer. The experimental points lay well on the calculated curve for the copolymerization of HEMA and MMA ($r_1 = 1.0$, $r_2 = 0.29$) in HEMA rich region.[5] The reactivity of the St macromonomer is not different from MMA except for the macromonomer-rich feed ratios, since the poly-St segment is remote from the reacting methacrylate group. Thus, the decrease in St content in the graftcopolymer is ascribed to the loss of St rich polymer soluble in diethyl ether, presumably because of the contaminated unreactive St prepolymer in the macromonomer. The purity of the graftcopolymer in Tables III and IV was checked by GPC and TLC. Typical GPC chromatograms are shown in Figure 2. By using UV and RI detectors, it was proved that PSt segment was evenly distributed in the whole polymer.

The results of the fractionation of the graftcopolymer are shown in Table V. Soxhlet extraction with cyclohexane removed trace amounts of PSt and further extraction with methanol removed considerable amounts of HEMA rich polymers. Thin layer chromatography was useful in characterizing the graftcopolymers. Figure 3 shows that the methanol insoluble fraction is not developed in TLC either by methanol or ethyl acetate, thus confirming the different behavior of the
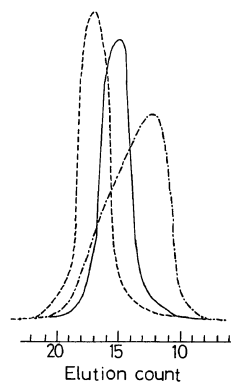

Figure 2. GPC chromatogram for graftcopolymers: ------, macromonomer (No. 341) $M_n = 4300$; ———, St–HEMA graftcopolymer (No. 3412) $M_n = 14000$, PSt (feed) 68.7 wt%; —·—, St–(HEMA-co-MMA) graftcopolymer (No. 3414) $M_n = 44300$, PSt (feed) 20.0 wt%, HEMA (feed) 39.9 wt%.
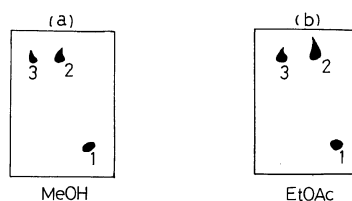

Figure 3. TLC chromatogram for ternary graftcopolymers. (a): 1, PHEMA; 2, PMMA; 3, G3615 (MeOH insoluble part). (b): 1, PSt; 2, PMMA, 3, G3615 (MeOH insoluble part).

fractions from PSt, poly(MMA) or poly(HEMA). From the above results, the formation of the graftcopolymer was established. The purity of the graftcopolymer was higher in the case of a lower HEMA feed ratio and a ternary system might be preferred.

A hydrophobic graftcopolymer was prepared using perfluoroalkyl acrylate as the comonomer. Benzotrifluoride was used as the solvent in the polymerization and the polymer was precipitated into cyclohexane. PSt macromonomer of $M_n = 4900$ (No. 381) was copolymerized with an equal amount of perfluoroalkyl acrylate at 60°C, using 1 mol% of AIBN. After five days, the yield of the graftcopolymer was 60%. The graftcopolymer was soluble in THF, diethyl ether, warm cyclohexane and benzotrifluoride, indicating the amphiphilic nature of the copolymer; the foaming solution resulted from the high surface activity of the graftcopolymer. GPC measurement with UV and RI detectors proved that the graftcopolymer was free of unreacted macromonomer and that the distribution of the PSt branches was uniform throughout the graftcopolymer. M_n was 40,000 and the PSt content was 50.9 wt%. The observed difference in solubility between the copolymer and the homopolymer suggests the formation of the graftcopolymer, but further study seems necessary to find a means for the purification of the graftcopolymer.

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