Synthesis of Acrylic Macromonomers by Free-Radical-Initiated Polymerization. Conversion to Comblike Copolymers†

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ABSTRACT: A versatile procedure was developed for synthesis of acrylic comblike copolymers in three steps: (1) Hydroxyl-terminated oligomers were synthesized from methyl methacrylate, butyl acrylate, and glycidyl (meth)acrylate by free-radical-initiated addition polymerization using a functional chain-transfer agent, 2-mercaptoethanol, and very low initiator levels. (2) The oligomers were converted to macromonomers by reaction with reaction with isocyanatoethyl methacrylate. (3) The macromonomers were polymerized by free-radical initiation. Conditions during the first step must be carefully selected to minimize formation of bifunctional materials, which could cause gelation during the third step. A variety of structures can be made such as comblike copolymers with homopolymer tines or comblike homopolymers with copolymer tines. Functional groups can be introduced by copolymerizing glycidyl (meth)acrylate into the macromonomer. Assignment of comblike structures is not rigorously proven but is strongly supported by the synthetic route and by DSC, FT-IR, and chromatographic data.

Introduction

Comblike polymers are distinguished from graft polymers by the close and regular spacing of their side chains and from star polymers by the attachment of the side chains to a polymeric chain rather than to a central core. They share with star polymers the useful property of having much lower solution and bulk viscosities than linear polymers of similar molecular weight. Comblike copolymers are generally synthesized by polymerization of macromonomers—oligomers or polymers that contain a single polymerizable group on one end. Macromonomers have been synthesized by a variety of techniques[1] involving anionic,[2] cationic,[3] and group-transfer[4,5] polymerization.

Until recently there have been few reports of synthesis of macromonomers by routes involving free-radical chain polymerization. If such a process could be developed, it would open a straightforward route to a very wide variety of comblike polymers. Free-radical chain polymerization is relatively easy to carry out, and it can be used to polymerize many monomers, including functional monomers, that are difficult or impossible to polymerize by anionic, cationic, or group-transfer methods. A major obstacle to the development of such a process is the difficulty of attaching a polymerizable group to one end of the great majority of macromonomer molecules while suppressing the formation of molecules having two or more reactive groups. A macromonomer contaminated with polyfunctional material can be expected to gel when polymerization is attempted.

In 1986 Albrecht and Wunderlich showed that these difficulties can be overcome in the case of poly(methyl methacrylate).[6] They synthesized PMMA macromonomers with $\bar{M}_w$'s of 6500–23 000 by free-radical polymerization of MMA in the presence of a functional chain-transfer agent, 2-mercaptoethanol (2-ME), followed by fractionation and reaction of the monohydroxy functional products with isocyanatoethyl methacrylate (IEM). Polymerization of these macromonomers yielded comblike polymers with $\bar{M}_w$'s on the order of 10^6 as determined by light scattering. The necessity of fractionation may limit the utility of this method to relatively high T_g materials. Thus it would be desirable to find a procedure that does not involve fractionation.

Here we report the development of such a procedure, one which appears to be relatively general with respect to monomer selection and product T_g. It will be shown that comblike copolymers of methyl methacrylate (MMA), butyl acrylate (BA), and glycidyl methacrylate (GMA) can be synthesized by a three-step procedure that can be idealized as follows:

step 1

$$\underset{1\text{ mol}}{I^\bullet} + \underset{1000\text{ mol}}{M} + \underset{100\text{ mol}}{HOXSH} \rightarrow \underset{1\text{ mol}}{IMMMMMMMMMMH} + \underset{98\text{ mol}}{HOXSMMMMMMMMMMH} + \text{termination products}$$

step 2

$$HOXSMMMMMMMMMMH + CH_2{=}C(Me)COOYN{=}C{=}O \xrightarrow[IEM]{} CH_2{=}C(Me)COOYNHCOOXSMMMMMMMMMMH$$

macromonomer

step 3

$$CH_2{=}C(Me)COOYNHCOOXSMMMMMMMMMMH + I^\bullet \rightarrow \text{comblike copolymer}$$

[$I^\bullet$ = initiator, M = mixed monomers, X and Y = $-CH_2CH_2-$]

The first step, macromonomer synthesis, was performed under the following conditions: (1) solution polymerization in toluene at 108–110 °C or in methyl isobutyl ketone (MIBK) at 80–90 °C, (2) monomer-starved conditions, (3) low levels of initiator and high levels of chain-transfer

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Table I
Molecular Weight and Conversions of Hydroxyl-Terminated Homopolymers and Copolymers

mole ratios, monomers/ 2-ME/AIBN	convn, wt %	$\bar{M}_w$ (GPC)	$\bar{M}_n$ (GPC)	PDI (GPC)	$\bar{M}_n$ (theor)[a]
-1000[b]/100/1	83	1.6×10^3	9.8×10^2	1.65	1.6×10^3
-1000[b]/50/1	60	3.1×10^3	2.1×10^3	1.48	3.2×10^3
-1000[c]/100/1	100	1.9×10^3	1.0×10^3	1.87	2.1×10^3
-1000[c]/50/1	99	3.6×10^3	1.7×10^3	2.11	4.1×10^3
-1000[d]/100/1	77	1.8×10^3	8.7×10^2	2.08	1.9×10^3
-1000[d]/50/1	75	3.5×10^3	1.8×10^3	1.88	3.8×10^3
-1000[e]/100/1	91	1.8×10^3	9.5×10^2	1.94	1.8×10^3
-1000[e]/50/1	72	3.4×10^3	1.6×10^3	2.05	3.6×10^3
-1000[f]/100/1	69	1.8×10^3	8.1×10^2	2.18	1.7×10^3
-1000[f]/50/1	66	3.4×10^3	1.4×10^3	2.40	3.4×10^3

[a] Theoretically calculated $\bar{M}_n$. [b] MMA. [c] BA. [d] MMA/BA 30/70. [e] MMA/BA 50/50. [f] MMA/BA 70/30.

agent (for example, a 1000/100/1 or a 1000/50/1 mol ratio of monomer/2-ME/initiator), and (4) postheating of the product to 140–175 °C in most cases. These conditions were chosen to minimize termination by combination, which is expected to lead to bifunctional materials, and to virtually eliminate unreacted initiator before addition of IEM. Deviation from these conditions generally gave materials that gelled during attempted polymerization of the macromonomer.

By adhering to these conditions a variety of structures including homopolymeric backbones with copolymeric tines and copolymeric backbones with homo- and copolymeric tines were synthesized.

Experimental Procedures

Materials. Reactants were 97–99% grade obtained or purchased from commercial sources and were used without further purification. Methyl methacrylate (MMA) and butyl acrylate (BA) were obtained from Rohm & Haas. 2-Mercaptoethanol (2-ME), glycidyl methacrylate (GMA), glycidyl acrylate (GA), 2,2-dimethyl-1,3-propanediol (NPG), 1,4-butanediol (1,4-BD), and pyromellitic dianhydride were purchased from Aldrich. Isocyanatoethyl methacrylate (IEM) was obtained from Dow Chemical Co. "Aromatic 100" is a mixed alkylbenzene solvent, boiling range 155–177 °C, supplied by Exxon Chemical Co.

Synthesis of Hydroxyl-Terminated Homo- and Copolymers of Methyl Methacrylate (MMA) and Butyl Acrylate (BA). Solutions of 2-mercaptoethanol (2-ME) and 2,2′-azobis(isobutyronitrile) (AIBN) in the monomer(s) having a monomer/2-ME/AIBN mole ratio of 1000/100/1 or 1000/50/1 were added continuously during 2.5 h to a three-necked reaction flask containing refluxing toluene in a N_2 atmosphere. The weight of toluene approximately equaled the weight of reactants. Stirring and refluxing were continued throughout the addition and for 4 h thereafter. A sample was withdrawn to gravimetrically estimate conversion of monomer to nonvolatile (NV) material; conversion varied somewhat but typically ran 60–80%. The resulting solution was gradually heated to 160–170 °C with stirring under a nitrogen purge to volatilize solvent and unreacted monomers and to decompose residual initiator. The FT-IR spectra had substantial peaks at about 3500 cm^{-1} (OH stretching) and were otherwise consistent with the assigned structures.

The conversions of all polymerizations and data for molecular weight determinations by gel permeation chromatography (GPC) [weight-average molecular weight ($\bar{M}_w$), number-average molecular weight ($\bar{M}_n$), and the polydispersity index (PDI = $\bar{M}_w/\bar{M}_n$)] of various hydroxyl-terminated homo- and copolymers of methyl methacrylate and butyl acrylate are shown in Table I.

Synthesis of Hydroxyl-Terminated PMMA with Hydroxyl Number Determinations of the Product and of Distilled Volatiles. An apparatus as described above was used. A solution of MMA (100 g, 1.0 mol), 2-ME (7.96 g, 0.1 mol), and AIBN (2.00 g, 0.012 mol) was dropped into the flask containing toluene (100 g) at reflux temperature (108–110 °C) under a nitrogen purge with mechanical stirring for 2 h. The reaction was allowed to proceed for an additional 4 h. To the PMMA solution was added Aromatic 100 (103 g), and the reaction temperature was then gradually raised to 170 °C to distill the unreacted monomer and solvent. A total of 158 g of the solvent mixture was distilled and was designated S-1. To the polymer solution in the reaction flask was added 158 g of toluene, and this mixture was designated P-1.

In a similar manner, a second batch of hydroxyl-terminated PMMA was prepared by using MMA (100 g, 1.0 mol), 2-ME (7.96 g, 0.1 mol), and AIBN (0.20 g, 1.2×10^{-3}) in toluene. The distilled solvent mixture was designated S-2. The hydroxyl-terminated PMMA solution was designated P-2.

Hydroxyl numbers of solvent distillates S-1 and S-2, of polymers P-1 and P-2, were determined by the pyromellitic dianhydride/dimethylformamide titration method.[7] The method was checked with commercial 2,2-dimethyl-1,3-propanediol ("neopentyl glycol", NPG; 97% pure) and 1,4-butanediol (1,4-BD; 99% pure). Results are given in Table II.

Table II
Hydroxyl Numbers of PMMA and Distilled Solvent

samples	determined OH no.	theoretical OH no.
NPG	54.7	52
NPG	54.3	52
1,4-BD	48.8	49
1,4-BD	49.6	49
S-1	0.9	0
S-2	0	0
P-1	52	53
P-2	55.5	53
toluene	0	0

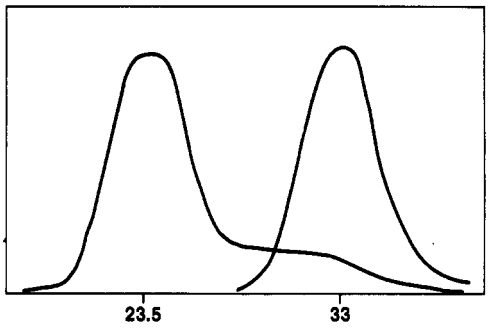


Figure 1. GPC traces of a hydroxyl-terminated poly(MMA/BA) copolymer and of a comblike copolymer made from it (acrylate/2-ME/AIBN mole ratio 1000/100/1).

Synthesis of MMA and BA Homo- and Copolymer Macromonomers. To the above solutions were added isocyanatoethyl methacrylate (IEM) and dibutyltin dilaurate (DBTDL); the amount of IEM was a 10 mol % excess over the amount of 2-ME used in the above synthesis, and the concentration of DBTDL was 4.7×10^{-4} wt %. The total concentration of reactants in xylene was about 30 wt %. The solutions were heated at 55 °C with stirring overnight. Disappearance of the FT-IR peak at 3500 cm^{-1} (OH) and appearance of peaks at 3350 (NH) and 1640 cm^{-1} (C=C) indicated complete reaction.

Synthesis of Comblike Homo- and Copolymers. AIBN (2.5 mol/L) was added to the above solutions (about 30 wt %), and the solutions were heated with stirring under N_2 to 60 °C. The solutions became very viscous within 5–10 min; heating was continued briefly, and the solutions were cooled. The solutions often gelled when lower AIBN concentrations or higher temperatures were used. Typical GPC traces are shown in Figures 1 and 2.

Synthesis of Butyl Acrylate/Glycidyl Methacrylate Copolymer. Thermal Stability of Copolymer. An apparatus as described above was used. A solution of BA (50 g, 0.39 mol), glycidyl methacrylate (GMA) (50 g, 0.34 mol), and AIBN (0.50 g, 3.05×10^{-3} mol) was added during 2 h to a three-necked round-bottomed flask containing 100 g of MIBK at 85–90 °C. After

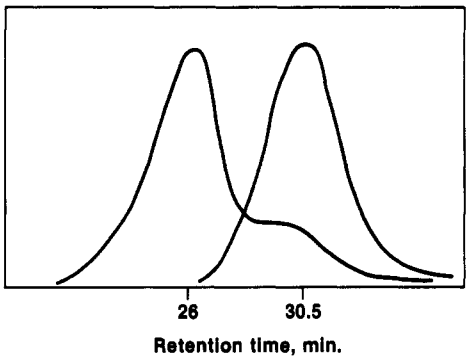


Figure 2. GPC traces of a hydroxyl-terminated poly(MMA/BA) copolymer and of a comblike copolymer made from it (acrylate/2-ME/AIBN mole ratio 1000/50/1).

monomer addition, the reaction was held for an additional 1 h. AIBN (0.1 g, 6.09×10^{-4} mol) was added, and reaction was continued at 85–90 °C for 4 h. Monomer conversion was 100% as determined gravimetrically. IR (neat film) showed a peak at 909 cm^{-1}, indicating the presence of epoxy groups. Solvent (87 g of MIBK) was removed by distillation at temperatures of up to 175–180 °C, and the temperature was maintained at 175–180 °C for 1 h. The IR spectrum (neat film) showed that the peak at 909 cm^{-1} was still present and no peak at 3500 cm^{-1} (OH stretching) had appeared.

Synthesis of Hydroxyl-Terminated BA/GA Copolymers and Conversion to Macromonomers. In the synthesis of BA/glycidyl acrylate (GA) copolymers with a weight ratio of 83/17, a solution of BA (100 g, 0.781 mol), GA (21.07 g, 0.156 mol), 2-ME (3.731 g, 0.047 mol), and AIBN (0.154 g, 9.3×10^{-4} mol) was dropped into a three-necked round bottomed flask containing 123 g of MIBK at 85–90 °C during 2 h, and the resulting solution was stirred at this temperature for 4 h. Monomer conversion was 88% as determined gravimetrically. The copolymer was further diluted with MIBK so that the total concentration was 30 wt %. IR (neat film) had a peak at 3500 cm^{-1}, indicating the presence of hydroxyl groups. GPC $\bar{M}_w = 1.7 \times 10^3$, $\bar{M}_n = 1.1 \times 10^3$, and PDI = 1.6.

Similarly, a BA/GA copolymer with a weight ratio of 67/33 was synthesized by using the same acrylate/2-ME/AIBN ratio. Monomer conversion was 84%. GPC $\bar{M}_w = 3.3 \times 10^3$, $\bar{M}_n = 1.2 \times 10^3$, and PDI = 2.7.

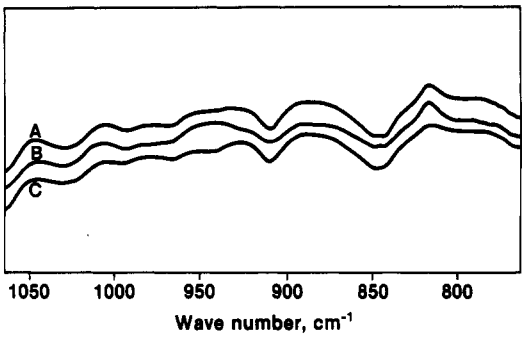
The above hydroxyl-terminated copolymers were reacted with IEM essentially as described above to yield macromonomers designated M-A (BA/GA ratio 83/17) and M-B (BA/GA ratio 67/33).

Synthesis of Epoxy Functional Comblike Copolymers. Solutions of MMA homopolymer macromonomer and macromonomer M-A (described above) in MIBK (30 wt %) were mixed in a weight ratio of 40/60. AIBN was added to the above mixture so that the concentration of AIBN was 0.025 M, and the solutions were stirred until homogeneous and then kept at 95 °C for 4 h to yield a solution of functionalized comblike copolymer C-A.

Comblike copolymer B was prepared similarly from 40 parts of MMA homopolymer macromonomer and 60 parts of macromonomer M-B.

Reaction of Macromonomer M-B with 2-ME. To a 30% solution of 30 g of macromonomer B in MIBK (containing 2.31×10^{-2} mol of GA) was added 2-ME (1.86 g, 2.33×10^{-2} mol). The mixture was heated to 65 °C for 17 h. GPC MW was the same as that of the original macromonomer B, and the disappearance of the peak at 1640 cm^{-1} (C=C) in the IR spectrum (neat film) suggests that the double bonds were consumed by 2-ME. The peaks at 909 and 3500 cm^{-1} in the IR (neat film) indicate the presence of epoxy and hydroxyl.

Polymerization of Macromonomer M-B with AIBN and a Test of the Reactivity with 2-ME. To a 30% solution of 30 g of macromonomer M-B in MIBK (containing 2.31×10^{-2} mol of GA) was added AIBN (0.18 g, 1.1×10^{-3} mol), and a FT-IR spectrum was taken (spectrum 1). The mixture was heated at 85 °C for 2 h, and the FT-IR spectrum was taken (spectrum 2). The increased GPC MW and the disappearance of the peak at



A: spectrum 1 minus spectrum 2
B: spectrum 1 minus spectrum 3
C: spectrum 1 minus spectrum 4

Figure 3. FT-IR subtraction spectra.

1640 cm^{-1} (C=C) in the FT-IR (neat film) spectra indicated that polymerization had occurred.

To the above copolymer solution was added 2-ME (2.34 g, 2.94×10^{-2} mol) followed by heating with mechanical stirring to 85 °C. FT-IR (neat film) spectra were recorded after 2 h (spectrum 3) and 24 h (spectrum 4). Comparison of expanded subtraction spectra among the spectrum 1 minus spectrum 2 (spectrum A), spectrum 1 minus spectrum 3 (spectrum B), and spectrum 1 minus spectrum 4 (spectrum C) shown in Figure 3 indicates that the peak intensity at 909 cm^{-1} remained unchanged.

Test Procedures. Differential scanning calorimetry (DSC) was effected with a Du Pont Model 990 thermal analyzer using samples that had been heated under N_2 for 2 h to remove volatiles. Heating rate was 10 °C/min. T_g was taken as the onset of the endothermic deflection. Gel permeation chromatography (GPC) was effected by Waters 100A, 500A, 1000A, and 10 000A columns in series; the solvent was tetrahydrofuran, and a Waters Model R401 refractive index detector was used. IR spectra were determined by Mattson Cygnus 25 FT-IR or Perkin-Elmer sodium chloride Model 137 spectrophotometers. Hydroxyl numbers were determined by the pyromellitic dianhydride/dimethylformamide titration method and are expressed in milligrams of KOH per grams of solid resin.[7] Nonvolatile percent (NV%) was determined by heating weighed (to the nearest milligram), approximately 0.5-g samples (solids basis) in an aluminum weighing dish (53-mm diameter) in a Blue M convection oven at 150 °C to constant weight (30–40 min).

Results and Discussion

Step 1. Conditions for synthesis of hydroxyl-terminated polymers were devised after a good deal of trial and error; they seem reproducible except that monomer conversions vary. This variation is attributable to the unusually low levels (0.07 wt %) of AIBN used in this study to minimize formation of nonfunctional chains and concentration of residual AIBN; 0.5–1.0 wt % of AIBN is commonly used. Five such materials made with 1000/100/1 monomer/2-ME/AIBN ratios had $\bar{M}_n$'s of 800–1000 and $\bar{M}_w\bar{M}_n$ of 1.6–2.2 as measured by GPC; conversions were 69–100%. Five similar materials prepared with 1000/50/1 ratios had $\bar{M}_n$'s of 1400–2100 and $\bar{M}_w/\bar{M}_n$ of 1.5–2.4 at conversions of 60–99%. The results are shown in Table I.

As shown in Table I, the concentration of 2-ME chain-transfer agent has a pronounced effect on the molecular weight. When the proportion of 2-ME was doubled by changing the (meth)acrylate/2-ME/AIBN mole ratios of 1000/50/1 and 1000/100/1, $\bar{M}_n$ was approximately halved. However, values of $\bar{M}_n$ determined by GPC were, in every case, lower than theoretically calculated for an ideal chain-transfer process. Calculations were made by the method of O'Brien and Gornick,[8] which involves several assumptions. When a chain-transfer constant of 0.62 is assumed for 2-ME, the calculated degree of polymerization ($\bar{P}_n$) is 16 for the 1000/100/1 ratio and 32 for the 1000/50/1 ratio.

The theoretical $\bar{M}_n$ values in Table I were obtained by multiplying theoretical $\bar{P}_n$'s by the molecular weight of the monomers or by the average M of the monomer mixtures. Calculations of theoretical $\bar{M}_n$ by the method of Gray[9] gave similar conclusions.

Several factors probably contribute to the fact that measured $\bar{M}_n$'s are roughly half of theoretical expectations. They include (1) occurrence of other chain-transfer reactions, such as chain transfer to solvent, (2) less than 100% conversion, and (3) the possibility of systematically low measurements by GPC.

The relatively severe distillation conditions (170 °C) at the end of step 1 were intended to decompose unreacted AIBN and to volatilize all solvent and unreacted monomer and 2-ME (bp 157 °C). To determine the actual fate of 2-ME, the hydroxyl numbers of distilled solvent and of polymer were determined in selected cases. The data are shown in Table II, along with data for tests used to validate the hydroxyl number determination method. The actual hydroxyl numbers are low (0.9 mg of KOH/g) for distillate S-1 and 0 for distillate S-2, and virtually all of the 2-ME can be accounted for in polymers P-1 and P-2. In view of the very low levels of 2-ME in the distillates, the low $\bar{M}_n$'s of the products, the known high reactivity of mercaptans as chain-transfer agents, and the fact that hydroxyl numbers of the products account for the –OH groups but not the –SH groups of 2-ME, it is reasonable to assume that virtually all of the 2-ME present at the outset becomes covalently bound to polymer during step 1. As will be shown, any residual 2-ME will be consumed during step 2 by reaction with the isocyanate groups of IEM or by Michael addition to its double bond.

The validity of hydroxyl number determination was confirmed by analyzing commercial 2,2-dimethyl-1,3-propanediol (NPG); 97% pure) and 1,4-butanediol (1,4-BD; 99% pure). As shown in Table II, good agreement was found in both reactants despite concern about possible errors in measurement of sterically hindered hydroxyl groups noted by Lu.[10] Substantial deviation from the procedures recommended for step 1 generally afforded precursors that caused gelation during step 3. The recommended procedures yield macromonomers that do not gel, although they become very viscous in 30 wt % solution. Some bifunctional macromonomer is presumably present and causes bridging of comblike structures, but its level is apparently low enough that gelation can be avoided.

Steps 2 and 3. Conversion of the hydroxyl-terminated polymers to macromonomers by reaction with IEM and polymerization of the macromonomers is relatively straightforward. Disappearance of the FT-IR peak at 3500 cm^{-1} (OH) and appearance of peaks at 3350 (NH) and 1640 cm^{-1} (C=C) indicate that the expected step 2 reaction occurred. Viscosity increase and chromatographic data indicate the facility of step 3.

Characterization of Products. GPC traces (Figure 1) of a hydroxyl-terminated poly(MMA/BA) (70/30 w/w) polymer derived from a monomer/2-ME/AIBN ratio of 1000/100/1 and of the comblike copolymer made from it are typical. It can be seen from these traces that low molecular weight macromonomers were converted to higher molecular weight products, presumably comblike copolymers. In general, retention times of the hydroxyl-terminated (step 1) products were 30–35 min while those of the comblike copolymers (step 3) were 22–26 min. A small to modest amount of low molecular weight material was always present in the comblike copolymers. It is attributable to the presence of a nonreactive fraction in the product of step 1. A modest fraction of the step 1 polymerization is inevitably initiated by species other than the free radical of the 2-mercaptoethanol chain-transfer agent; lacking hydroxyl groups, this fraction cannot form macromonomer. This explanation is supported by the fact that areas under these tails are consistently larger when comblike polymers were prepared from stage 1 products made with (meth)acrylate/2-ME/AIBN mole ratios of 1000/50/1 (Figure 2) than when they were prepared from materials made with a mole ratio of 1000/100/1 (Figure 1). When the amount of 2-ME used was reduced by half, the average chain length may about double but the number of nonreactive chains initiated by AIBN is about constant; thus, the weight fraction of nonreactive chains from this source would about double. In addition, a higher proportion of chain transfer to solvent might occur.

Gel permeation chromatography calibrated with linear polystyrene standards indicated $\bar{M}_n$'s on the order of 10^5 for the comblike copolymers made in this study, but these values cannot be regarded as valid measurements of absolute molecular weight. Quite likely they are too low. It is well-known[6,11] that the hydrodynamic volume of highly branched polymers is much lower than that of similar polymers of the same molecular weight. Thus correlation of GPC retention times of comblike polymers with those of linear standards can be expected to understate the molecular weight of the comblike materials. For example, Albrecht and Wunderlich measured the molecular weight of their comblike PMMA as 10^6 by light scattering but only 4.5×10^4 by GPC.

Retention times were shorter for polymers made at lower (60 vs 90 °C) stage-three polymerization temperatures, indicating that, on a relative basis, lower temperatures favor higher molecular weight comblike copolymers. A recent kinetic study of free-radical copolymerization of macromonomers showed that the reactivity of a growing chain with a macromonomer end toward a second macromonomer decreases as molecular weight increases.[12] This observation is attributed to a kinetic excluded-volume effect. In the context of the present study, this result is consistent with the assignment of comblike structures for the third-step products but suggests that further study of how reaction conditions affect molecular weight is warranted.

With the objective of making comblike copolymers bearing functional groups as potential cross-linking sites, we investigated copolymerization of glycidyl acrylate into the hydroxyl-terminated precursors. Somewhat milder reaction conditions, detailed above, were used in order to minimize the potential for side reactions. One side reaction of concern is the possibility of reaction of the thiol group of 2-ME with the oxirane ring of the glycidyl (meth)acrylate, an occurrence that would increase functionality of the hydroxyl-terminated precursor and probably lead to gelation in step 3. Mercaptans are known to react readily with epoxy resins under some circumstances.[13]

Several experiments were performed to estimate the facility of the undesired ring-opening side reaction. FT-IR peaks at 909 and 3500 cm^{-1} were used to monitor the possible epoxy ring-opening reactions with 2-ME. Subtraction spectra in the 909-cm^{-1} region are shown in Figure 3. Treatment of macromonomer M-B (BA/GA = 67/33) with equivalent (to epoxy ring content) amounts of 2-ME at 65 °C for 17 h caused no detectable change of the peak at 909 cm^{-1} but disappearance of the peak at 1640 cm^{-1} (C=C), indicating that 2-ME undergoes Michael addition to the double bond under these conditions but does not rapidly attack the epoxy group. To eliminate the com-

Table III
T_g of Selected Hydroxyl-Terminated Precursors and of Comblike Copolymers

description	composition (wt ratio)	T_g, °C
PMMA precursor	OH-terminated PMMA, M_n ca. 1000	40
PBA precursor	OH-terminated PBA, M_n ca. 1000	−60
BA/GA precursor A	OH-terminated BA/GA 83/17 copolymer	−40
BA/GA precursor B	OH-terminated BA/GA 67/33 copolymer	−35
comblike	MMA/BA 30/70, copolymer tines	−15
comblike	MMA/BA 50/50, copolymer tines	8
comblike	MMA/BA 70/30, copolymer tines	24
comblike	MMA/BA 30/70, homopolymer tines	−44, 39
comblike	MMA/BA 50/50, homopolymer tines	−43, 29
comblike	MMA/BA 70/30, homopolymer tines	−49, 39
comblike	MMA homopolymer, BA/GA 83/17 copolymer	−22
comblike	MMA homopolymer, BA/GA 67/33 copolymer	−17
control	MMA/BA/HEMA 40/40/20 random copolymer	26

plication of the double bond, comblike copolymer C-B (contains 2.31×10^{-2} mol of GA) was exposed to a slight excess of 2-ME (2.94×10^{-2} mol) at 85 °C for 24 h. Again, the subtraction spectra indicated little or no effect on the epoxy ring (spectrum C in Figure 3). We conclude that the chain-transfer reaction must be much faster than the oxirane addition reaction. If chain transfer consumes virtually all of the 2-ME, there is no need for concern about the ring-opening side reaction by residual mercaptan.

A second side reaction of concern is the possibility that hydroxyl groups of the step 1 product might react with oxirane groups. The thermal stability of this material at 175 °C indicates that this reaction would be negligible at temperatures (85–90 °C) used for polymerization and that the material can withstand postheating (to remove solvent and decompose AIBN) at 170 °C.

Availability of different copolymer macromonomers opens possibilities for synthesis of a wide variety of structures involving copolymerization in the first stage, the third stage, or both. For example, copolymerization in the first stage and homopolymerization in the third will yield a relatively uniform comblike copolymer. On the other hand, if two dissimilar macromonomers from the first stage are blended and then polymerized in the third stage, a comblike copolymer with homopolymer tines can be expected. To illustrate the possibilities, several types of comblike copolymers were synthesized and studied by DSC, with the results shown in Table III.

As can be seen from Table III, comblike MMA/BA copolymers made from single copolymeric precursors display a single T_g, while comblike copolymers of similar overall composition made from mixtures of homopolymeric precursors ("comblike copolymers with homopolymer tines") display two T_g's, one presumably related to the T_g of the BA precursor and the other to the T_g of the MMA precursor. However, only the lower T_g's could be detected in the comblike copolymers with a homopolymeric MMA tine and copolymeric BA/GA tines. The T_g assignments of 29–40 °C for PMMA and −43 to −60 °C for PBA tines are reasonable in view of the low molecular weights of these oligomers. Lin reported[14] that PMMA samples having $\bar{M}_n$'s of 3300, 33 000, and 250 000 had T_g's of 66, 99, and 104 °C, respectively.

Numerous applications for comblike copolymers with homo- or copolymer tines can be envisaged. For example, it was shown[15] that the comblike copolymers with PMMA and PBA tines are capable of compatibilizing the two incompatible PMMA and PBA homopolymers. Thus, with an appropriate structural design, the comblike copolymers can be used as compatibilizers. As was discussed by Albrecht and Wunderlich, the comblike homopolymer with PMMA tines having a $\bar{M}_w$ of 10^6 measured by light scattering showed solution behavior comparable to linear PMMA of $\bar{M}_w = 5.5 \times 10^4$. This suggests that the comblike molecules behaved like a highly compact molecule with relatively low levels of intramolecular entanglements. Thus comblike polymers and copolymers may be useful in applications, such as coatings and adhesives, where low-viscosity solutions of high molecular weight polymers are often desired. With the successful preparations of epoxy-functionalized comblike copolymers, a variety of crosslinkable polymers for high solid coatings and adhesives can be envisaged.

Conclusions

A versatile procedure for the synthesis of short-chain acrylic macromonomers by a free-radical-initiated chain-transfer process has been demonstrated. These materials can be converted to an almost limitless variety of comblike polymers and copolymers. While the process requires careful control of conditions, it appears adaptable to large-scale production. Comblike copolymers with dissimilar homopolymer tines display two T_g's. Reactive functional groups can be incorporated by copolymerization of glycidyl acrylate. Assignment of comblike structures is not rigorously proven but is strongly supported by the synthetic route and by DSC, FT-IR, and chromatographic data.

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Registry No. (IEM)(BA) (graft copolymer), 132622-53-8; (IEM)(MMA) (graft copolymer), 107391-61-7; (IEM)-(BA)(MMA) (graft copolymer), 132622-54-9; (BA)(GMA) (copolymer), 26660-36-6; (MMA)(MA) (graft copolymer), 132622-55-0.