Graft Copolymers by Combined Anionic and Cationic Polymerizations Based on the Homopolymerization of a Bifunctional Monomer

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ABSTRACT: The bifunctional monomer 2-(vinyloxy)ethyl methacrylate (VEMA) was polymerized both anionically and cationically. Using 1,1-diphenylhexyllithium (DPHL) as initiator, tetrahydrofuran (THF) as solvent and the low temperature of −60 °C, the C═C double bond of the methacryloyl group of VEMA underwent smoothly anionic polymerization, without cross-linking or side reactions. The polymer had a controlled molecular weight and a narrow molecular weight distribution (M_w/M_n = 1.06−1.12). On the other hand, the C═C double bond of the vinyloxy group of VEMA can undergo cationic polymerization. A polymer with controlled molecular weight and narrow molecular weight distribution (M_w/M_n = 1.11−1.13) was prepared using 2-[1-acetoxyethoxy]ethyl methacrylate (**4**)/$EtAlCl_2$ as initiator in the presence of THF, a weak Lewis base. Two methods were employed to prepare graft copolymers. (A) The anionically prepared polymer of VEMA was separated from solution after quenching the polymerization and purified by freeze-drying; then the vinyloxy groups of the side chains were allowed to react with trifluoroacetic acid to generate a macroinitiator, which finally induced the cationic graft polymerization of isobutyl vinyl ether (IBVE). This procedure yielded a graft copolymer with a polymethacrylate backbone and poly(IBVE) side chains containing a small amount of the IBVE homopolymer. (B) The anionic polymerization of **4** was carried out in THF without quenching, to produce a solution of macroinitiator. Then, in contrast to the first method, the polymer was not separated and toluene and IBVE were introduced into the system. Further, the cationic graft polymerization of IBVE was induced by adding an activator ($EtAlCl_2$). The THF, which was used as solvent in the anionic polymerization of **4**, acted as a Lewis base in the cationic polymerization step. This procedure yielded a pure graft copolymer with controlled molecular weight and narrow molecular weight distribution (M_w/M_n = 1.15−1.17), consisting of a polymethacrylate backbone and poly(IBVE) side chains.

Introduction

In recent years, great attention was paid to graft copolymers, because of their unique molecular architecture, particular morphology and increased number of applications.[1−5] They have been widely used for the preparation of compatibilizers for polymer blends,[6−11] membranes for separation of gases or liquids,[12−14] hydrogels,[15] drug deliverers,[16] thermoplastic elastomers,[17] etc. A number of methods have been employed for their synthesis, such as the macromonomer method,[18−20] radiation-induced polymerization,[21−23] ring-opening olefin methathesis polymerization,[24] polycondensation reaction[25] and iniferter-induced polymerization.[26] However, the living polymerization technique is undoubtedly most suitable for the preparation of well-defined graft copolymers, in which both the backbone and the side chains possess designed molecular weights and narrow molecular weight distributions and the position, the number of side chains, and the composition of the graft copolymer can be controlled. Se and co-workers[27] prepared a well-defined block−graft copolymer using the living anionic polymerization method. A block copolymer consisting of polystyrene and poly((4-vinylphenyl)dimethylvinylsilane) and living polyisoprene were first prepared separately, and their coupling reaction generated a graft copolymer. In this method, the unreacted polyisoprene had to be removed by repeated dissolution and precipitation. Recently, we have prepared a graft copolymer consisting of a polymethacrylate backbone and poly(alkyl vinyl ether) side chains,[28] by using the anionic polymerization of 1-(isobutoxy)ethyl methacrylate followed by the cationic polymerization of alkyl vinyl ether. In that method, the poly(1-(isobutoxy)ethyl methacrylate) had to be isolated from its tetrahydrofuran (THF) solution and purified carefully before it was used as macroinitiator for the cationic polymerization of alkyl vinyl ether. In the present paper, an improved continuous method is reported for the synthesis of a similar graft copolymer with controlled molecular weight and narrow molecular weight distribution, in which the above lengthy purification is no longer needed.

2- (Vinyloxy)ethyl methacrylate (VEMA, **1** in Scheme 1) is a bifunctional monomer possessing an anionically as well as a cationically polymerizable C═C double bond. The C═C double bond located in the α position of the carbonyl is expected to undergo anionic polymerization and a functional polymer (**2**, in Scheme 1; abbreviated as PMA), having a cationically polymerizable C═C double bond in each side chain, to be formed. On the other hand, the C═C double bond of the ester group of VEMA is expected to undergo cationic polymerization to generate another functional polymer (**3** in Scheme 1; abbreviated as PVE) with a reactive methacryloyl group in each repeating unit. Obviously, two different functional polymers can be obtained from the same monomer, by its selective anionic or cationic polymerization.

A graft copolymer was prepared by two different routes. In route A (Scheme 2), PMA (**2**) was allowed to react with trifluoroacetic acid to generate a dormant macroinitiator (**5**, in Scheme 2). In route B, the vinyl

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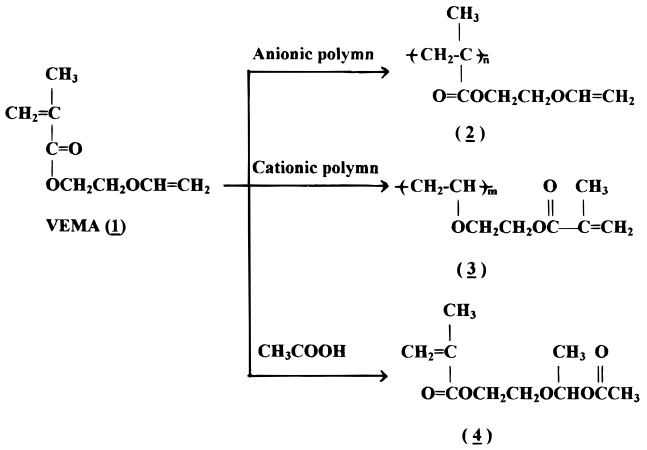
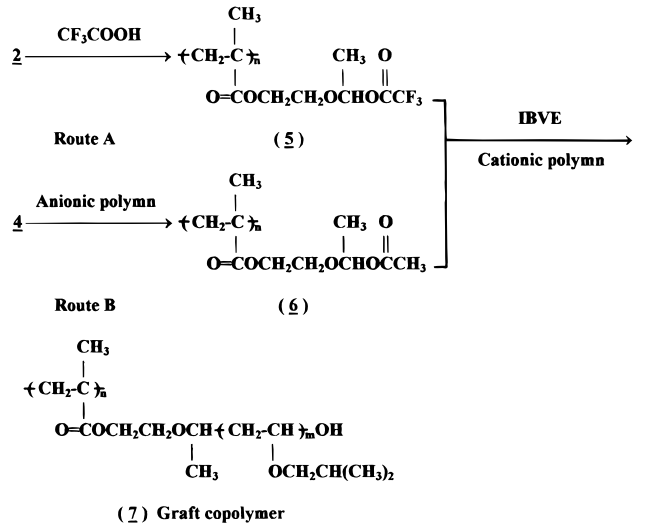
Scheme 1



Scheme 2



of the ester group of VEMA was selectively reacted with acetic acid to produce a new monomer, 2-[1-acetoxyethoxy]ethyl methacrylate (**4**, in Scheme 1) which generated, via anionic polymerization, the dormant macroinitiator (**6**, in Scheme 2) with a molecular structure similar to that of **5**. The side chains of both **5** and **6** were activated by Lewis acids[29−31] to generate partly dissociated carbocations, which induced the cationic polymerization of vinyl ether. This yielded a graft copolymer (**7**, in Scheme 2) with a polymethacrylate backbone and poly(alkyl vinyl ether) side chains.

Experimental Section

Materials. Tetrahydrofuran (THF) was dried with CaH_2 under reflux for more than 24 h, distilled, purified in the presence of naphthalene sodium, and finally distilled from a solution of (1,1-diphenylhexyl)lithium (DPHL) just before use. Toluene was washed with concentrated sulfuric acid and then with water, dried over $MgSO_4$, and distilled twice over CaH_2 before use. Et_2O was dried over CaH_2 and distilled in the presence of $LiAlH_4$. Hexane was first dried and distilled over CaH_2 and then distilled from a solution of *n*-BuLi. Isobutyl vinyl ether (IBVE; Aldrich, 99%) was washed with 10% aqueous sodium hydroxide solution and then with water, dried overnight with potassium hydroxide, and distilled twice over CaH_2 prior to polymerization.[29,31] 1,1-Diphenylethylene (DPE, Aldrich, 97%) was doubly distilled over CaH_2 and then distilled in the presence of triphenylmethyllithium under reduced pressure.[32] Lithium chloride (Aldrich, 99.99%) was dried at 120 °C for 24 h and dissolved in THF.[33] *n*-BuLi (Aldrich, 1.6 M solution in hexane), $ZnCl_2$ (Aldrich, 1.0 M solution in diethyl ether), and $EtAlCl_2$ (Aldrich, 1.8 M solution in toluene) were diluted with purified hexane, diethyl ether and toluene, respectively. 1-Isobutoxyethyl trifluoroacetate (IETA) and 1-isobutoxyethyl acetate (IEA) were prepared by the addition reactions between IBVE and trifluoroacetic acid (Aldrich, 99%) or acetic acid (Aldrich, 99.8%), respectively.[29−31]

Table 1. Anionic Polymerization of VEMA[a]

no.	$[n\text{-BuLi}]_0$, mM	$[DPE]$, mM	$[LiCl]$, mM	$[M]_0$, M	$10^{-3} M_n$ calcd	$10^{-3} M_n$ obsd[b]	M_w/M_n[b]
PMA-1	33.3	40.0	66.7	0.43	2.25	2.61	1.10
PMA-2	22.2	26.6	0	0.43	3.26	3.39	1.24
PMA-3	16.7	20.0	0	0.43	4.26	4.65	1.23
PMA-4	16.7	20.0	33.3	0.43	4.26	4.49	1.08
PMA-5	13.5	16.2	27.0	0.52	6.24	6.72	1.06
PMA-6	14.5	17.4	29.0	0.65	7.23	7.42	1.10
PMA-7	10.0	12.0	20.0	0.52	8.35	9.21	1.07
PMA-8	5.1	6.2	11.0	0.65	20.2	23.2	1.12

[a] Polymerization was carried out in THF at −60 °C for 1 h. The monomer conversion was 100% in each case. [b] Determined by GPC.

Syntheses of 2-(Vinyloxy)ethyl Methacrylate (VEMA, 1 in Scheme 1) and 2-[1-Acetoxyethoxy]ethyl Methacrylate (4, in Scheme 1). VEMA was prepared through the reaction between 2-chloroethyl vinyl ether (Aldrich, 99%) and sodium methacrylate (Aldrich, 99%) under reflux with stirring, in the presence of small amounts of a phase transfer catalyst (tetrabutylammonium iodide) and an inhibitor (4-*tert*-butylcatechol).[34−36] **4** was synthesized by the addition reaction between VEMA and acetic acid (Scheme 1). In a 100 mL round-bottom flask equipped with a condenser and a magnetic stirrer, 21.0 g (0.14 mol) VEMA and a small amount of 4-*tert*-butylcatechol were introduced under the protection of nitrogen. After 4-*tert*-butylcatechol had dissolved and the temperature had been raised to 70 °C, acetic acid (8.1 g, 0.14 mol; Aldrich, 99.8%) was dropwise added with a syringe. The reaction lasted 5 h at 70 °C and the crude product was distilled under reduced pressure (bp: 65−66 °C/1.0 Torr; yield 86%). Prior to polymerization, the monomer was doubly distilled over CaH_2. As shown later in Figures 2A and 5A, the chemical shifts and their intensities in the ^1H NMR spectra of the prepared VEMA and **4** are consistent with their molecular structures.

Anionic Polymerization of VEMA. All polymerizations, anionic, cationic and graft copolymerizations, were carried out in a 100 mL round-bottom glass flask under an overpressure of nitrogen with magnetic stirring. The anionic polymerization of VEMA was performed in THF at −60 °C with or without LiCl. After THF, DPE, and a THF solution of LiCl were added with dry syringes, the flask was cooled to −45 °C and *n*-BuLi (in hexane) was introduced. The deep red color of DPHL appeared at once, and the reaction between *n*-BuLi and DPE was allowed to continue for 15 min. Then, the system was cooled to −60 °C and the polymerization reaction was induced by the addition of a prechilled THF solution of VEMA to the above DPHL solution. After a selected time, the reaction was quenched with a small amount of methanol and the polymer solution was poured into a methanol−water mixture to precipitate the polymer. The polymer was reprecipitated by pouring its THF solution into the above mixture and finally dried in vacuum overnight.

Cationic Polymerization of VEMA. IETA, IEA and **4** were separately used as initiators for the cationic polymerization of VEMA, which was induced by adding, with a dry syringe, a solution of $ZnCl_2$ in Et_2O or of $EtAlCl_2$ in toluene to a toluene solution of VEMA and an initiator at 0 or 25 °C (see Table 2). The polymerization was terminated with methanol containing a small amount of ammonia. The quenched reaction mixture was washed with a 10% aqueous sodium thiosulfate solution (for $ZnCl_2$) or with a dilute hydrochloric acid (for $EtAlCl_2$) and then with water, evaporated to dryness under reduced pressure, and vacuum-dried to obtain the polymer.

Addition of Trifluoroacetic Acid to the Vinyls of the Side Chains of PMA and the Preparation of A Graft Copolymer by a Discontinuous Method. PMA prepared

Table 2. Cationic Polymerization of VEMA[a]

no.	initiator		activator		time, h	$[M]_0$, M	$10^{-3}M_n$		M_w/M_n[b]
	name	amt, mM	name	amt, mM			calcd	obsd[b]	
PVE−1	IETA[c]	33.0	$ZnCl_2$	16.7	3	0.40	1.89	1.81	1.29
PVE−2	IETA[c]	16.0	$ZnCl_2$	8.3	4	0.40	3.90	3.29	1.30
PVE−3	IEA[d]	25.0	$ZnCl_2$	13.0	8	0.40	2.50	2.41	1.38
PVE−4	IEA[d]	16.0	$ZnCl_2$	7.0	8	0.40	3.90	3.32	1.47
PVE−5	**4**[e]	15.0	$EtAlCl_2$	45.0	3	0.32	3.33	3.35	1.30
PVE−6[f]	**4**[e]	33.0	$EtAlCl_2$	120	24	0.40	1.89	1.62	1.13
PVE−7[f]	**4**[e]	15.0	$EtAlCl_2$	90.0	24	0.32	3.33	3.46	1.11

[a] Polymerization was carried out in toluene at 0 °C for PVE-1 to PVE-4 or 25 °C for PVE-5 to PVE-7. The yields of polymers were quantitative in all cases. [b] Determined by GPC. [c] IETA: 1-(isobutoxy)ethyl trifluoroacetate. [d] IEA: 1-(isobutoxy)ethyl acetate. [e] **4**: 2-(1-acetoxyethoxy)ethyl methacrylate (see Scheme 1). [f] Adding THF as Lewis base, [THF] = 1.5 M.

by the anionic polymerization of VEMA was freeze-dried from its benzene solution for 8 h and then vacuum-dried for more than 10 h. The purified toluene or a mixture of toluene and CCl_4 was introduced into the flask that contained the dried PMA. After the polymer had dissolved and the solution had been cooled to 0 °C, trifluoroacetic acid was added and the addition reaction was allowed to last for 1.5 h. Subsequently, toluene and IBVE were introduced and the graft copolymerization was induced by the addition of a Et_2O solution of $ZnCl_2$. The termination of the reaction and the purification of the obtained copolymer were carried out as described above for the cationic polymerization of VEMA.

Anionic Polymerization of 4 and the Preparation of a Graft Copolymer by a Continuous Method. The anionic polymerization of **4** was carried out as for VEMA. However, poly(**4**) was not separated from its THF solution, to which toluene and IBVE were added. After the temperature was raised to 25 °C, a toluene solution of $EtAlCl_2$ was introduced to start the graft copolymerization. The termination reaction and the purification of the produced copolymer were carried out as described for the cationic polymerization of VEMA.

Measurements. ^{1}H NMR spectra were recorded in $CDCl_3$ or CD_3OD on a VXR-400 spectrometer. M_n and M_w/M_n of the polymer were determined by gel permeation chromatography (GPC) on the basis of a polystyrene calibration curve. The GPC measurements were carried out using THF as solvent, at 30 °C, with a 1.0 mL/min flow rate and a 1.0 cm/min chart speed. Three polystyrene gel columns (Waters, 7.8 × 300 mm; two Linear, Part No. 10681, and one HR 4E, Part No. 44240) were used, which were connected to a Waters 515 precision pump.

Results and Discussion

VEMA was polymerized by either anionic or cationic polymerization to produce soluble polymers.[37,38] However, its living cationic polymerization was achieved only when the HI/I_2 initiating system was employed. Aoshima et al.[36] carried out the cationic polymerization of VEMA with HI/I_2 as initiator, in toluene, at −15 to −40 °C and obtained a polymer with controlled molecular weight and narrow molecular weight distribution. In the present paper, both the anionic and cationic polymerization of VEMA were carried out under different conditions than those previously used.

Anionic Polymerization of VEMA. LiCl has a positive effect on the anionic polymerization of the acrylic monomers,[39,40] because a μ-type complex[41] is formed between LiCl and the propagating site, which, by prevention of side reactions, markedly narrows the molecular weight distribution. In the present paper, this polymerization technique is employed in order to prepare a functional polymer (PMA) of VEMA, with controlled molecular weight and narrow molecular weight distribution.

The initiator, DPHL, was synthesized via the reaction of *n*-BuLi with DPE in the ratio $[DPE]/[n\text{-BuLi}]_0 = 1.2$ (Table 1), at −45 °C, for 15 min. The anionic polymerization was carried out in THF at −60 °C in the presence ($[LiCl]/[n\text{-BuLi}]_0 = 2$) or absence of LiCl. As shown in Table 1, VEMA can be anionically polymerized, with or without LiCl addition. However, the addition of LiCl controls the anionic polymerization of VEMA. The determined molecular weight of PMA is in good agreement with that calculated by assuming complete monomer conversion and that each initiator molecule generates a polymer chain (PMA-4 to PMA-8, in Table 1). The molecular weight distribution is narrow, nearly monodisperse. Figure 1 compares the GPC curves. Obviously, the sharp peak (curve B) of PMA-7 prepared in the presence of LiCl is comparable to that of polystyrene standard (curve C, $M_n = 10\,000$, $M_w/M_n = 1.06$) and the molecular weight distribution of PMA-7 ($M_n = 9210$, $M_w/M_n = 1.07$) is much narrower than that of PMA-2 (curve A, $M_n = 3390$, $M_w/M_n = 1.24$), which was obtained in the absence of LiCl, even though the molecular weight of PMA-7 is larger. These results indicate that the anionic polymerization of VEMA in the presence of LiCl can proceed smoothly in a living manner without chain transfer or terminating reactions.

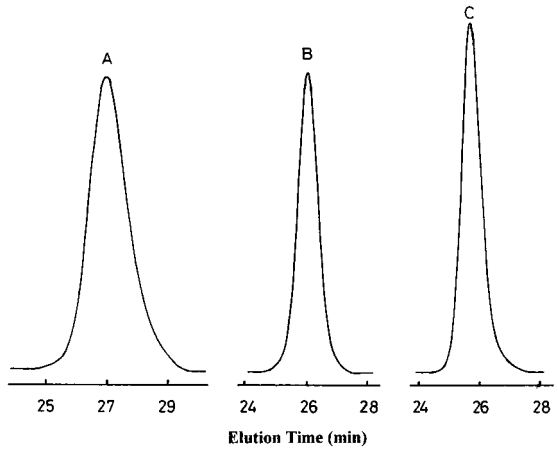


Figure 1. GPC traces of PMAs prepared in the absence (A, PMA-2 in Table 1, $M_n = 3390$, $M_w/M_n = 1.24$) or presence (B, PMA-7 in Table 1, $M_n = 9210$, $M_w/M_n = 1.07$) of LiCl and a standard polystyrene (C; Pressure Chemical Company, $M_n = 10\,000$, $M_w/M_n = 1.06$. Lot No. 70111).

Parts A and B of Figure 2 depict the ^{1}H NMR spectra of the monomer (VEMA) and its anionically obtained polymer (PMA), respectively. After polymerization, the peaks **a** and **b** corresponding to the α-methyl and C=C double bond of the methacryloyl group, shifted to 0.7−1.3 (**a′**) and 1.7−2.2 ppm (**b′**), respectively. However, the other absorptions including the C=C double bond of vinyloxy group (**e** and **f**) did not change. In addition, PMA is soluble in THF, benzene, toluene, chloroform, ethyl acetate, etc. Evidently, no cross-linking reaction occurred during the anionic polymerization of VEMA,

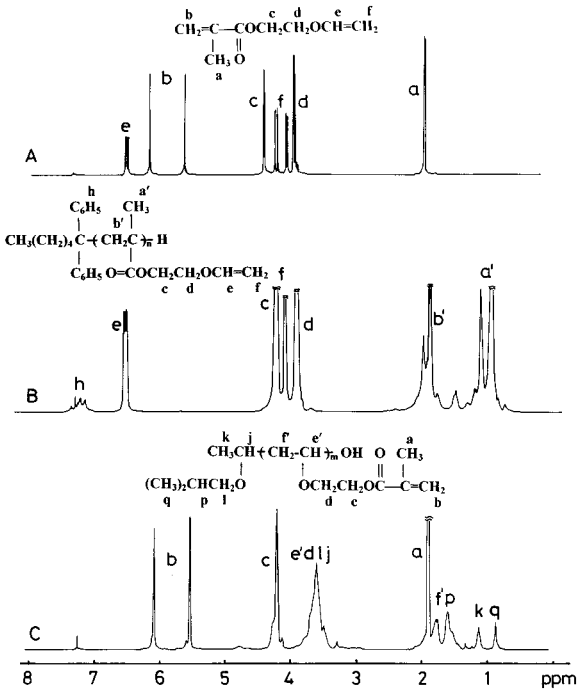


Figure 2. ^{1}H NMR spectra of VEMA (A), PMA (B, PMA-7 in Table 1) prepared by the anionic polymerization of VEMA and PVE (C, PVE-2 in Table 2) prepared by the cationic polymerization of VEMA.

and the PMA thus obtained is a functional polymer, with a vinyloxy group in each side chain.

Cationic Polymerization of VEMA. The living cationic polymerization of a number of vinyl monomers, such as alkyl vinyl ether, isobutylene, and styrene-type monomers, was already achieved.[42−45] Higashimura et al.[29−31] demonstrated that the adducts of acetic acid derivatives with alkyl vinyl ethers can induce the living cationic polymerizations of vinyl ethers in the presence of an activator, such as $ZnCl_2$ or $EtAlCl_2$. In the present paper, three similar adducts, 1-isobutoxyethyl trifluoroacetate (IETA), 1-isobutoxyethyl acetate (IEA) and 2-[1-acetoxyethoxy]ethyl methacrylate (**4**, in Scheme 1), were employed as initiators for the cationic polymerization of VEMA. The polymerization was carried out in toluene at 0 °C (for PVE−1 to PVE−4, in Table 2) or 25 °C (for PVE−5 to PVE−7, in Table 2), and the reaction was started by adding the activator ($ZnCl_2$ in Et_2O or $EtAlCl_2$ in toluene) to the toluene solution of VEMA and initiator. As shown in Table 2, VEMA can be cationically polymerized regardless of the initiator and activator used. However, the molecular weight distributions of the produced polymers are different. When IEA/$ZnCl_2$ initiating system was used, the molecular weight distribution of the polymer was broad (Figure 3A, PVE−4 in Table 2, M_n = 3320, M_w/M_n = 1.47). This happened because the Lewis acid employed, $ZnCl_2$, is too weak and the nucleophilicity of the counteranion ($^-OCOCH_3\cdots ZnCl_2$) too strong. However, when a very strong Lewis acid, $EtAlCl_2$, was used, the molecular weight distribution was also broad (Figure 3B, PVE−5 in Table 2, M_n = 3350, M_w/M_n = 1.30), because the counteranion ($^-OCOCH_3\cdots EtAlCl_2$) is too weakly nucleophilic. In contrast, when a weak Lewis base, THF, was added to the above system, a narrowly disperse polymer was obtained (Figure 3C, PVE−7 in Table 2, M_n = 3460, M_w/M_n = 1.11). In this case, the carbocation was suitably stabilized by the added base.[30,31]

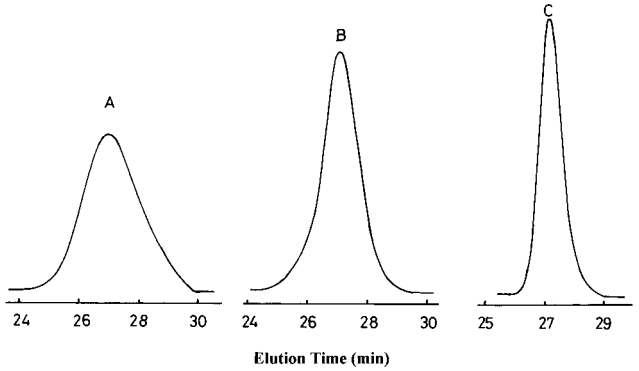


Figure 3. GPC traces of PVEs: (A) PVE-4 (in Table 2, M_n = 3320, M_w/M_n = 1.47) prepared by using IEA and $ZnCl_2$ as initiator and activator, respectively; (B) PVE-5 (in Table 2, M_n = 3350, M_w/M_n = 1.30) prepared by using **4** and $EtAlCl_2$ as initiator and activator in the absence of a Lewis base; (C) PVE−7 (in Table 2, M_n = 3460, M_w/M_n = 1.11) prepared by using **4**, $EtAlCl_2$, and THF as initiator, activator, and Lewis base, respectively.

The above cationic polymerization of VEMA demonstrates again that it is important to regulate the nucleophilic interaction between the growing carbocation and the counteranion ($^-OCOR\cdots MX_n$).

As depicted in Figure 2C, the ^{1}H NMR spectrum of the cationically obtained polymer (PVE) of VEMA is free of peaks **e** and **f** corresponding to the C=C double bond of vinyloxy group in the monomer (Figure 2A), but retains the absorptions (**a** and **b**) of methacryloyl groups.

PVE can be dissolved in THF, benzene, chloroform, etc. Thus, VEMA was selectively polymerized via the cationic polymerization of its vinyloxy group without any cross-linking during polymerization. The PVE thus obtained is a functional polymer, with a methacryloyl group in each repeating unit.

Consequently, two different functional polymers could be prepared from a unique monomer, VEMA, via anionic and cationic polymerization, respectively.

Synthesis of a Macroinitiator from PMA and the Graft Copolymerization via a Discontinuous Method. The preparation of a graft copolymer was first tried using a discontinuous route (route A in Scheme 2). PMA prepared by the anionic polymerization of VEMA was freeze-dried from its benzene solution and then vacuum-dried for more than 10 h. The addition reaction between the vinyloxy group of the dried PMA and trifluoroacetic acid was carried out in toluene at 0 °C for the ratio [CF_3COOH]/[C=C] = 1.1, for 1.5 h. After the addition reaction, the molecular weight of the polymer became larger (Table 3), the GPC curve of PMA disappeared (Figure 4A) and a new peak (Figure 4B) emerged in the high molecular weight region. This means that the addition reaction generated a new polymer (**5** in Scheme 2). **5** is a dormant macroinitiator for the cationic polymerization of alkyl vinyl ether, because each of its side chains has a structure similar to that of IETA, which was used as initiator for the cationic polymerizations of IBVE[31] and VEMA described above.

The cationic graft polymerization of IBVE to the macroinitiator **5** was carried out in toluene at 0 °C (Table 4). IBVE and $ZnCl_2$ (in Et_2O) were introduced into a toluene solution of **5** and the polymerization reaction was allowed to last for 3 h. As shown in Figure 4, the peak B of the macroinitiator (MI-2 in Table 3)

Table 3. Preparation of Macroinitiator from PMA[a]

						macroinitiator	
no.	amt of PMA-1[b], g	[C=C][c], M	[CF_3COOH], M	amt of toluene, mL	amt of CCl_4, mL	$10^{-3}M_n$[d]	M_w/M_n[d]
MI−1	0.44	0.14	0.16	20	0	3.82	1.13
MI−2	0.50	0.16	0.18	15	5	3.92	1.15

[a] The addition reaction was carried out at 0 °C for 1.5 h. [b] PMA-1 in Table 1: $M_n = 2610$, $M_w/M_n = 1.10$. [c] Concentration of repeating units in PMA. [d] Determined by GPC.

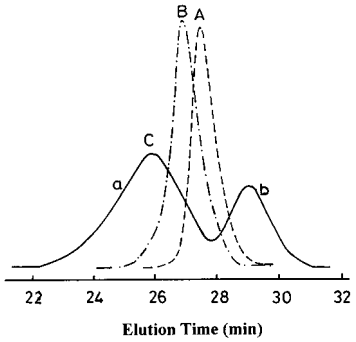


Figure 4. GPC traces for preparation of graft copolymers by a discontinuous method: (A) PMA (PMA-1 in Table 1, $M_n = 2610$, $M_w/M_n = 1.10$); (B) macroinitiator (MI-2 in Table 3, $M_n = 3920$, $M_w/M_n = 1.15$) prepared by the addition of trifluoroacetic acid to PMA-1; (C), after polymerization of IBVE (see GP-2 in Table 4), (a) a graft copolymer ($M_n = 9740$, $M_w/M_n = 1.37$), (b) a homopolymer of IBVE.

Table 4. Synthesis of Graft Copolymer by a Discontinuous Method[a]

					graft copolymer[c]	
no.	macro-initiator	$[I]_0$[b], mM	$[IBVE]_0$, M	$[ZnCl_2]$, mM	$10^{-3}M_n$[d]	M_w/M_n[d]
GP-1	MI-1[e]	56.4	0.28	28.0	9.32	1.39
GP-2	MI-2[e]	64.2	0.32	32.0	9.74	1.37

[a] Graft copolymerization was carried out in toluene at 0 °C for 3 h. Monomer conversion was 100% in each case. [b] Concentration of repeating units in macroinitiator. [c] Data corresponding to the graft copolymer, not including the homopolymer (see Figure 4). [d] Determined by GPC. [e] See Table 3.

disappeared completely after the graft copolymerization and two new peaks (C-a and C-b) emerged. Peak C-a corresponds to the produced graft copolymer, which has a much larger molecular weight (GP-2 in Table 4, $M_n = 9740$) than its macroinitiator (MI-2 in Table 3, $M_n = 3920$). On the other hand, Peak C-b with a low molecular weight ($M_n = 510$) was caused by an excess of trifluoroacetic acid. In the preparation of the macroinitiator, an excess of trifluoroacetic acid must be added to ensure a complete addition of trifluoroacetic acid to the vinyloxy group. Consequently, a graft copolymer, with a polymethacrylate backbone and poly(IBVE) side chains can be prepared by this discontinuous method. However, the homopolymer of IBVE had to be removed in order to obtain the pure graft copolymer. In addition, the graft copolymer had a broad molecular weight distribution ($M_w/M_n = 1.37-1.39$, Table 4) and PMA used for the preparation of the macroinitiator had to be purified carefully. To overcome these shortcomings, another continuous method was tried.

Anionic Polymerization of 4 and the Preparation of a Graft Copolymer by a Continuous Method. **4** (in Scheme 1) can be used not only as an initiator for the cationic polymerization of VEMA (as noted above), but can also undergo anionic polymerization, because of the presence of the electron-deficient C=C double bond in the methacryloyl group; the poly(**4**) thus obtained is expected to be a dormant macroinitiator for the cationic polymerization of IBVE (**6**, route B in Scheme 2). As shown in Table 5, the anionic polymerization of **4** was carried out under conditions similar to those used for the anionic polymerization of VEMA. In the presence of LiCl, the anionic polymerization of **4** proceeded smoothly, without side reactions. The molecular weight of the macroinitiator poly(**4**) (determined by injecting a small amount of the THF polymerization solution into the GPC) could be controlled and the molecular weight distribution was narrow. However, when we tried to separate the poly(**4**), after quenching the polymerization system with a methanol−water mixture, another polymer, poly(2-hydroxyethyl methacrylate), precipitated slowly in about 3 h, because of the elimination of 1-acetoxyethyl group ($^+CH(CH_3)$-$OCOCH_3$) of the side chains of poly(**4**). Parts A and B of Figure 5 depict the ^1H NMR spectra of **4** (Figure 5A) and of the precipitated polymer (Figure 5B). The absorptions (**e**, **f**, and **g**) due to the 1-acetoxyethyl groups disappeared completely, and were replaced by a new peak (**i**) in the spectrum of the precipitated polymer, which can be assigned to a hydroxyl group. These results indicate that, using the above procedure, poly(2-hydroxyethyl methacrylate) with a narrow molecular weight distribution can be prepared, but not the macroinitiator (**6** in Scheme 2) which can be further employed for graft copolymerization. However, fortunately, the graft copolymer could be prepared by a continuous method without the separation of the macroinitiator. The THF solution of the macroinitiator (MI-3 to MI-5 in Table 5) was not quenched; instead purified toluene and IBVE were added to the solution. The system remained transparent and no polymer precipitated. After the system was brought to room temperature (25 °C), an activator $EtAlCl_2$ (in toluene) was added and the cationic graft polymerization of IBVE was allowed to proceed for 4 h (Table 6). THF, which was used as solvent in the preparation of the macroinitiator, acted as a Lewis base which stabilized the carbocation in the cationic polymerization step. As shown in Figure 6, the GPC peak (A) of the macroinitiator (MI-5 in Table 5, $M_n = 5050$, $M_w/M_n = 1.06$) disappeared entirely after the graft copolymerization. A new single peak (B) due to the graft copolymer (GP-5 in Table 6, $M_n = 26\,800$, $M_w/M_n = 1.12$) emerged, and no peak belonging to the homopolymer remained. As shown in Table 6, the graft copolymers (GP-3, GP-4, and

Table 5. Preparation of Macroinitiator by the Anionic Polymerization of 4[a]

					$10^{-3}M_n$		
no.	$[n\text{-BuLi}]_0$, mM	[DPE], mM	[LiCl], mM	$[M]_0$, M	calcd	obsd[b]	M_w/M_n[b]
MI-3	26.4	31.7	64.0	0.37	3.27	4.04	1.09
MI-4	17.6	21.1	23.0	0.37	4.78	4.60	1.17
MI-5	15.0	18.0	30.0	0.34	5.11	5.05	1.06
MI-6	9.6	11.5	24.0	0.34	7.89	8.80	1.20

[a] Polymerization was carried out in THF at −60 °C for 1 h. The monomer conversion was 100% in each case. [b] Determined by GPC.

Table 6. Synthesis of Graft Copolymer by A Continuous Method[a]

						graft copolymer		
						10^{-4}Mn		
no.	macro-initiator	$[I]_0$,[b] mM	[IBVE], M	[$EtAlCl_2$], M	[THF], M	calcd	obsd[c]	M_w/M_n[c]
GP-3	MI-3[d]	92.6	0.62	0.11	2.0	1.66	1.65	1.17
GP-4	MI-4[d]	77.2	0.64	0.12	2.0	2.12	1.76	1.15
GP-5	MI-5[d]	66.1	0.66	0.15	1.8	2.73	2.68	1.16

[a] Graft copolymerization was carried out in toluene at 25 °C for 4 h. Monomer conversion was 100% in each case. [b] Concentration of repeating units in macroinitiator. [c] Determined by GPC. [d] See Table 5.

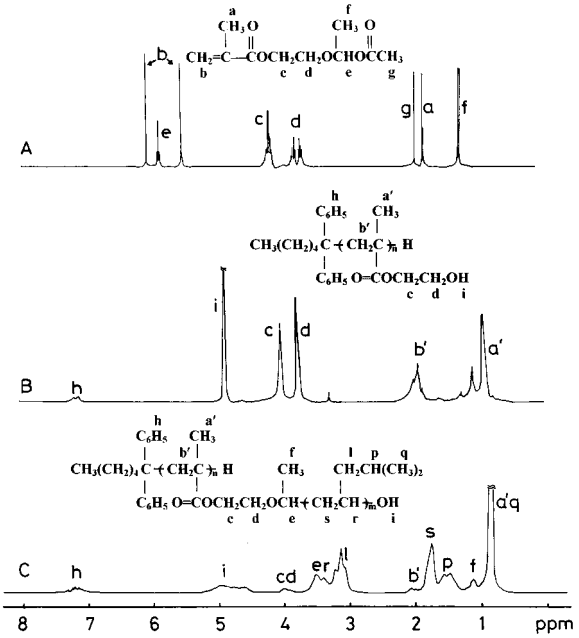


Figure 5. ^{1}H NMR spectra of **4** (A, dissolved in $CDCl_3$), poly(2-hydroxyethyl methacrylate) (B, dissolved in CD_3OD) obtained from MI-3 (Table 5) after elimination of its side chains by quenching with a methanol−water mixture, and graft copolymer (C, GP-3 in Table 6, dissolved in $CDCl_3$).

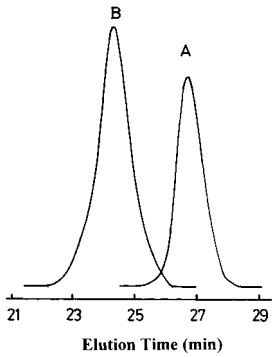


Figure 6. GPC traces for the preparation of a graft copolymer by the continuous method: (A) macroinitiator (MI-5 in Table 5, M_n = 5050, M_w/M_n = 1.06) prepared by the anionic polymerization of **4**; (B) graft copolymer (GP-5 in Table 6, M_n = 26800, M_w/M_n = 1.16).

GP-5) have controllable molecular weights and narrow molecular weight distributions (M_w/M_n = 1.15−1.17). These results indicate that all of the side chains of the macroinitiator were consumed in initiating the cationic polymerization of IBVE and that the side chains have an almost equal length.

In the ^{1}H NMR spectrum of the graft copolymer (Figure 5C, GP-3 in Table 6), besides the absorptions (**l**, **p**, **q**, **r**, **s**) of the poly(IBVE) side chains, the peaks (**b′**, **c**, **d**, **f**, **h**) corresponding to the main chain can be still observed. Both the GPC and ^{1}H NMR measurements indicate that a pure graft copolymer having controlled molecular weight and narrow molecular weight distribution, with a polymethacrylate backbone and poly(IBVE) side chains, was prepared by the continuous polymerization method.

Conclusion

2-Vinyloxyethyl methacrylate (VEMA) can be subjected to anionic or cationic polymerization to generate two kinds of functional polymers. Under the anionic polymerization conditions, the C═C double bond of the methacryloyl group of VEMA could be polymerized in THF, using DPHL as initiator, at −60 °C, in the presence of LiCl. A functional polymer, with a cationically polymerizable C═C double bond in each side chain, was thus obtained. The determined molecular weight of the polymer was in good agreement with that calculated assuming that each initiator molecule generates one polymer chain and its distribution was narrow (M_w/M_n = 1.06−1.12). On the other hand, the C═C double bond of the vinyloxy group of VEMA can undergo cationic polymerization. A polymer with controlled molecular weight and narrow molecular weight distribution (M_w/M_n = 1.11−1.13) was prepared using 2-[1-(acetoxy)ethoxy]ethyl methacrylate (**4**) /$EtAlCl_2$ as initiator in the presence of THF, a weak Lewis base. The polymer thus obtained had a reactive methacryloyl group in each repeating unit.

The vinyloxy groups of the side chains of the anionically prepared polymer of VEMA could react with trifluoroacetic acid to generate a macroinitiator, which induced the cationic graft polymerization of isobutyl vinyl ether (IBVE) in toluene in the presence of $ZnCl_2$. In this manner, a graft copolymer with a polymethacrylate backbone and poly(IBVE) side chains could be prepared. However, this graft copolymer contained a small amount of the IBVE homopolymer, because of the excess trifluoroacetic acid which had to be employed.

The anionic polymerization of **4**, which proceeds under conditions similar to those for the anionic polymerization of VEMA, produced a THF solution of a macroinitiator. After toluene and IBVE were introduced into the system, the addition of an activator ($EtAlCl_2$) induced the cationic graft polymerization of IBVE to the macroinitiator. The THF, which was used as solvent in the anionic polymerization of **4**, acted as a Lewis base in the cationic polymerization step. By this continuous method, a pure graft copolymer with controlled molecular weight and narrow molecular weight distribution (M_w/M_n = 1.15−1.17), consisting of a polymethacrylate backbone and poly(IBVE) side chains, could be prepared.

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