Polymers with Hydrophilic and Hydrophobic Polymeric Side Chains

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Received October 1, 1992; Revised Manuscript Received December 7, 1992

ABSTRACT: A comblike polymer with hydrophilic and hydrophobic side chains has been synthesized as follows: (1) A solution radical polymerization of dimethyl(hydroxyethyl)(4-vinylbenzyl)ammonium chloride and triphenyl(4-vinylbenzyl)phosphonium chloride generated a water-soluble copolymer. (2) The Wittig reaction converted the pendant phosphonium units to vinylstyrene units. (3) The addition of the surfactant Span-80 and of a hydrophilic monomer (acrylamide, sodium styrene sulfonate, or poly(ethylene glycol) diacrylate) followed by polymerization grafted a hydrophilic polymer to the vinylstyrene units. (4) The addition of a hydrophobic monomer (styrene, *n*-butyl acrylate) followed by polymerization grafted a hydrophobic polymer to vinylstyrene units protected by Span-80 molecules. ^{1}H NMR has been carried out to identify the presence of the vinylstyrene units after the Wittig reaction, and FT-IR and differential scanning calorimetry were used to study the polymers with hydrophilic and hydrophobic polymeric side chains. The compositions of the prepared polymers were determined by elemental analysis. The morphology and the microarea compositions of the polymers were investigated by employing scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) techniques. Their thermal properties were studied with a differential scanning calorimeter (DSC), and their affinities for various solvents were examined using swelling tests.

Introduction

Amphiphilic polymers constitute useful organic materials because they possess unique properties that result from the association of hydrophilic and hydrophobic moieties as blocks or grafting chains on the same polymer backbone.[1] They can be employed for immobilization of enzymes,[2] controlled drug release,[3] microencapsulation, and membranes for separation processes. The methods used in their synthesis include living polymerization sequential additions[4,5] and the modification of a hydrophilic (hydrophobic) polymer with a relatively low amount of a hydrophobic (hydrophilic) comonomer (1–5 mol %) in the micellar copolymerization.[6,7] Although the living polymerization method can provide well-defined molecular weights and architectures, it presents major difficulties in synthesis. The micellar copolymerization method can be employed mainly for the preparation of aqueous viscosity modifiers[8] or thermoplastic elastomers[9] because of the limited changes possible in the amount of comonomer.

In this paper a method that involves solution polymerization followed by concentrated emulsion polymerization is suggested for the preparation of polymers that possess hydrophilic and hydrophobic polymeric side chains. For illustrative purposes, the hydrophilic monomers dimethyl(hydroxyethyl)(4-vinylbenzyl)ammonium chloride (DMEVBAC), triphenyl(4-vinylbenzyl)phosphonium chloride (TPVBPC), acrylamide (AM), 4-sodium styrenesulfonate (NaSS), and poly(ethylene glycol) diacrylate (PEGDA) and the hydrophobic monomers styrene (ST) and *n*-butyl acrylate (*n*BA) have been used. First, a solution polymerization of DMEVBAC and TPVBPC in a mixture of water and tetrahydrofuran was carried out. This process leads to the water-soluble copolymer P(DMEVBAC–TPVBPC). The treatment of this copolymer with an aqueous solution of formaldehyde and NaOH converted its phosphonium units to vinylstyrene (VS) units (Wittig reaction), resulting in the copolymer P(DMEVBAC–VS). Further, Span-80 (an oil-soluble surfactant), one of the hydrophilic monomers (AM, PEGDA, NaSS), and the initiator K_2SO_8 were introduced into the system. The molecules of Span-80 are adsorbed on some of the VS units, and the vinyl groups that remain exposed become centers for the grafting of the hydrophilic monomers as hydrophilic polymeric chains. After polymerization, one of the hydrophobic monomers (ST, *n*BA) containing the initiator AIBN was introduced with stirring. A concentrated emulsion (an emulsion in which the volume fraction of the dispersed phase is large) in which the hydrophobic monomer probably constitutes the continuous phase is formed. The vinyl groups protected by Span-80 molecules become centers for grafting of the hydrophobic monomer as hydrophobic polymeric chains. Consequently, the resulting polymers are suggested to possess a comblike architecture with hydrophilic and hydrophobic polymeric side chains connected to a P(DMEVBAC–VS) backbone. These polymers will be denoted as P(DMEVBAC–VS//P (hydrophilic monomer)//P (hydrophobic monomer)), in which "//" symbolizes side chains.

A number of studies concerning the structure and properties of these polymers have been carried out. They include the ^{1}H NMR identification of the vinylstyrene units on P(DMEVBAC–VS), the infrared absorptions of the characteristic groups of the final polymers, swelling tests in various mixed solvents, and scanning electron microscopy (SEM) and differential scanning calorimetry (DSC) investigations of their morphology and thermal properties. The obtained materials display selective and cooperative swelling behaviors: they swell very little in ethanol but swell considerably in water; in addition, the polymer P(DMEVBAC–VS//PAM//PS) was found to swell much better in water–DMF–toluene than in water–DMF. These swelling characteristics suggest the possibility of preparing membranes that could be employed to remove water from mixtures of water and alcohol. The hydrophilic matrixes of PAM and PPEGDA are likely to be biocompatible, and therefore there exists potential for their use as carriers for drugs and enzymes.

Experimental Section

Materials. To remove the inhibitor *tert*-butylcatechol or HQ, styrene (Aldrich, 99%), butyl acrylate (Aldrich, 99%), and 4-vinylbenzyl chloride (Kodak, 99%) were passed through a

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packed column (Aldrich). Azobis(isobutyronitrile) (Kodak) was recrystallized from methanol before use. Triphenylphosphine (Aldrich, 99%), *N,N*-dimethylethanolamine (Aldrich, 99%), acrylamide (Aldrich, 99%), 4-styrenesulfonic acid sodium salt (Aldrich, Dip. A), poly(ethylene glycol) (Aldrich, average MW 400), acryloyl chloride (Aldrich, 98%), Span-80 (Fluka, sorbitan monooleate, HLB value 4.3), potassium persulfate (Aldrich, 99+%), and various solvents were used without further purification.

Instruments Employed. The infrared absorption spectra of the polymers were obtained with a Mattson Alpha Centauri FT-IR instrument. Proton nuclear resonance of the polymer P(BMEVBAC-VS) dissolved in DMSO-*d* was performed on a 300-MHz NMR instrument (GEM-300). The thermal characteristics of the prepared polymers were determined with a Perkin-Elmer differential scanning calorimeter (DSC) Model 2, under a nitrogen atmosphere, using a scanning rate of 20 deg/min. The viscosities of the water-soluble polymers P(DMEVBAC-TPVB-PC) were measured with an Ubbelohde viscometer, using water or a mixture of water and DMF (v/v = 1) as solvents. The morphologies of the final polymers were investigated with scanning electron microscopy (SEM, Hitachi S-800). Energy dispersive spectroscopy (EDS) analysis was performed with a PGT/IMIX system. The elemental analyses for N, P, O, and S were carried out by Quantitative Technologies, Inc. (Bound Brook, NJ).

Preparations. Synthesis of Triphenyl(4-vinylbenzyl)-phosphonium Chloride (TPVBPC). Triphenylphosphine (26.2 g, 100 mmol) was dissolved in 30 mL of DMF at 40 °C with stirring, and 4-vinylbenzyl chloride (15.3 g, 100 mmol) was added to the solution. The mixture was stirred at 40–45 °C overnight and then cooled to 10–5 °C. White crystals precipitated when about 30 mL of ethyl ether were introduced into the cooled mixture. The crude product was recrystallized by dissolving in $CHCl_3$ followed by precipitation with ether. After vacuum drying, 34.4 g of white solid was obtained.

Synthesis of Dimethyl(hydroxyethyl)(4-vinylbenzyl)-ammonium Chloride (DMEVBAC). *N,N*-Dimethylethanolamine (3.56 g, 40 mmol) was dissolved in 15 mL of DMF. After this solution was cooled to 10–5 °C in an ice-water bath, 4-vinylbenzyl chloride (6.24 g, 41 mmol) was added dropwise with magnetic stirring and the system was kept under stirring at the same temperature for about 30 min more. White crystals precipitated which were washed with stirring in 30 mL of ethyl ether and filtered in a Büchner funnel. This operation was repeated three times. After vacuum drying, 6.5 g of white powder was obtained. Because this compound is hygroscopic and polymerizes easily, its storage in a dry and cold environment was necessary.

Synthesis of the Water-Soluble Copolymer Poly(dimethyl(hydroxyethyl)(4-vinylbenzyl)ammonium chloride-*co*-triphenyl(4-vinylbenzyl)phosphonium chloride) [P(DMEVBAC-TPVBPC]. Three mole ratios of DMEVBAC to TPVBPC were employed in the synthesis (Table I). In one of them, DMEVBAC (2.47 g, 10 mmol), TPVBPC (4.24 g, 10.2 mmol), and AIBN (30 mg) were added to a mixture of THF and water (15 mL/10 mL) present in a glass tube. The tube was sealed with a rubber septum and subjected to ultrasonic mixing for 5 min under Ar bubbling. The initial suspension was thus transformed into a clear solution, which was subjected to polymerization at 50 °C for about 2 days. An aqueous polymer solution separated at the bottom of the tube, from which, after introducing 40 mL of THF with stirring, a polymer gel precipitated. This gel was purified twice by dissolution in water followed by precipitation with THF, and finally was vacuum dried at 60 °C. A brittle polymer (6.0 g) was thus obtained.

Synthesis of Poly(dimethyl(hydroxyethyl)(4-vinylbenzyl)ammonium chloride-*co*-4-vinylstyrene) [P(DMEVBAC-VS)]. A fine powder of P(DMEVBAC-TPVBPC) (3.0 g, containing 5.0 mmol of TPVBPC groups) was dissolved with stirring, under an Ar atmosphere, in a formaldehyde aqueous solution (10 mL, 37 wt %) held in a 50-mL flask. After the flask was placed into a cold water bath (10–5 °C), 1 mL of an aqueous solution of NaOH (50 wt %) was introduced dropwise with stirring, and the stirring was continued for an additional 2 h. The obtained white mixture was diluted with 70 mL of water and about 10 mL of HCl (2 N) and allowed to stay overnight for the precipitation of the reaction byproduct $Ph_3P{=}O$. About an 80-mL solution of P(DMEVBAC-VS) in water with a pH = 8.5 decanted; it contained about 22 mg of polymer/mL.

Preparation of the P(DMEVBAC-VS) Samples for Proton Nuclear Magnetic Resonance Measurements. A 10-mL solution of P(DMEVBAC-VS) in water (pH = 7) was extracted with chloroform three times (3 × 5 mL) to remove the organic impurities. The aqueous phase was allowed to evaporate overnight at room temperature. The precipitated solid was vacuum dried and then dissolved in DMSO-*d* for the NMR analysis.

Anchoring Poly(acrylamide) and Poly(styrene) to P(DMEVBAC-VS)—Preparation of P(DMEVBAC-VS//PAM//PS). In a 150-mL round-bottom flask, a solution of P(DMEVBAC-VS) in water (20 mL, containing about 440 mg of polymer), acrylamide (1.82 g, 25 mmol), $K_2S_2O_8$ (7–8 mg), and Span-80 (0.8 g) was introduced with stirring. The flask was sealed with a rubber septum and filled with Ar. When the flask was placed in a 40 °C water bath, a gel was formed after 35–40 min. To this gel cooled to room temperature was added dropwise with vigorous stirring (ca. 600 rpm) styrene (3 mL, 25 mmol) containing 22 mg of AIBN. A concentrated emulsion was thus generated, which was polymerized at 40–45 °C for 48 h. The polymer was cut into small pieces and stirred in water for 24 h with intermittent changing of water, the liquid was removed in a Büchner funnel, and the solid was extracted with $CHCl_3$–benzene (v/v = 1) in a Soxhlet apparatus for 24 h and finally dried in vacuum.

Anchoring Poly[(PEG)diacrylate] and Poly(styrene) to P(DMEVBAC-VS)—Preparation of P(DMEVBAC-VS//PPEGDA//PS). In a 150-mL flask, poly(ethylene glycol) (5 g, average MW = 400) and dry triethylamine (2.55 g, 25 mmol) as an acid acceptor were mixed and then cooled to 10–5 °C under an Ar atmosphere. Acryloyl chloride (2.3 g, 25 mmol) was added dropwise with magnetic stirring. Because the reaction of the tertiary amine with HCl is exothermic, the esterification of PEG with acryloyl chloride must be carried out at a low temperature in order to avoid the polymerization of the acryloyl groups. After the addition of acryloyl chloride, the system became a paste which was dissolved into a 20-mL aqueous solution of P(DMEVBAC-VS). After $K_2S_2O_8$ (7–8 mg) and Span-80 (0.8 g) were added, the system was emulsified by stirring for about 10 min. The emulsion was polymerized at 40 °C for 6 h under the protection of Ar. To this polymerized emulsion, cooled to room temperature was added dropwise with vigorous stirring (ca. 600 rpm) 3 mL of styrene containing 20 mg of AIBN. A concentrated emulsion was thus obtained which was polymerized at 40–45 °C for 48 h under an Ar atmosphere. The purification of the polymer was carried out as for P(DMEVBAC-VS//PAM//PS).

Anchoring Poly(4-sodium styrenesulfonate) and Poly(styrene) to P(DMEVBAC-VS)—Synthesis of P(DMEVBAC-VS//PNaSS//PS). 4-Styrenesulfonic acid sodium salt (5.3 g, 25 mmol), Span-80 (0.8 g), and $K_2S_2O_8$ (7–8 mg) were introduced with stirring into a 20 mL solution of P(DMEVBAC-VS) in water. The system was polymerized at 40 °C for 1.5 h under an Ar atmosphere. Styrene (3 mL) containing 22 mg of AIBN was added dropwise into this polymerized system with vigorous stirring (ca. 600 rpm). A yellow concentrated emulsion was obtained which was polymerized at 40–45 °C for 48 h. The purification of the polymer was carried out as for P(DMEVBAC-VS//PAM//PS).

Anchoring Poly(acrylamide) or Poly(4-sodium styrenesulfonate) and Poly(*n*-butyl acrylate) to P(DMEVBAC-VS)—Synthesis of P(DMEVBAC-VS//PAM//P*n*BA) and P(DMEVBAC-VS//PNaSS//P*n*BA). The preparation procedure is as for the synthesis of P(DMEVBAC-VS//PAM//PS) and P(DMEVBAC-VS//PNaSS//PS), butyl acrylate (5 mL, 35 mmol) replacing styrene.

Swelling Test. In order to examine the swelling behavior of the polymers, mixtures of water–ethanol, water–DMF–toluene, and water–DMF were employed. Polymer solids were accurately weighed (W_o) and introduced into the solvent mixture for 24 h at room temperature. The swollen solids were taken out, the liquid adhered to their surface was carefully wiped and then their weights (W_s) were determined. The swelling was calculated with the expression $(W_s - W_o)/W_o$.

Scheme I
Preparation of the Polymer P(DMEVBAC-VS)

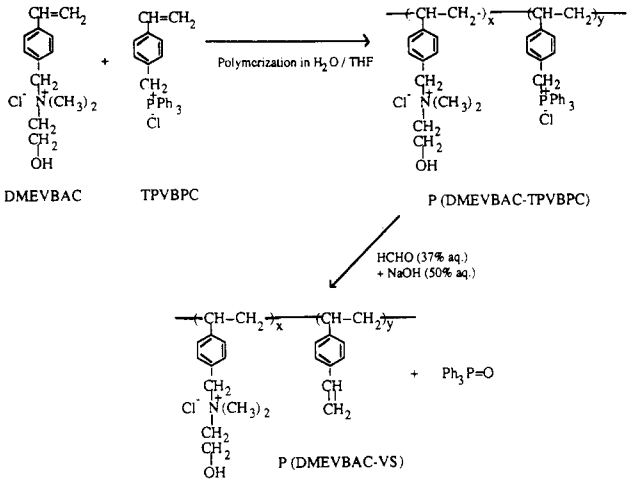

Table I
Characterization of the Water-Soluble Copolymer P(DMEVBAC-TPVBPC)

copolymer	DMEVBAC/TPVBPC[a] (mol ratio)	elemental anal. (mmol/g of polymer) N	P	N/P (mol ratio)	intrinsic viscosity [η] (mL/g) water	DMF/water (v/v = 1/1)
P_1	0.6	1.03	1.67	0.62	927	613
P_2	1.0	1.56	1.48	1.05	1144	738
P_3	1.8	1.92	1.06	1.81	1371	870

[a] The mole ratios of the monomers in the feedstock of solution polymerization; 10.2 mmol of TPVBPC was used.

Results and Discussion

Characterization of the Water-Soluble Copolymer P(DMEVBAC-TPVBPC). The substituents in the two monomers, DMEVBAC and TPVBPC, are expected to have comparable effects on the double-bond reactivity in copolymerization. For this reason, their copolymerization is likely to result in a statistical copolymer P(DMEVBAC-TPVBPC) (Scheme I). Table I shows that the proportions of ammonium N to phosphonium P units in the polymer chain are almost the same as those in the feedstock (for three different mole ratios of DMEVBAC to TPVBPC in the feedstock, which are denoted as P_1, P_2, and P_3).

The viscosity measurements show that when the N/P ratio in the copolymer chains is increased, the viscosities of their solutions in both water and water–DMF mixture increase, the one in water being larger than that in water–DMF. This is as expected, because, the DMEVBAC unit being more hydrophilic than the TPVBPC unit, the polymer chain becomes more extended in water with increasing N/P ratio. As a result, the viscosity increases. When the medium becomes less hydrophilic, by introducing for instance DMF in water, the viscosity of the solution will decrease compared to that in water because the polymer chains become more coiled in a less hydrophilic environment.

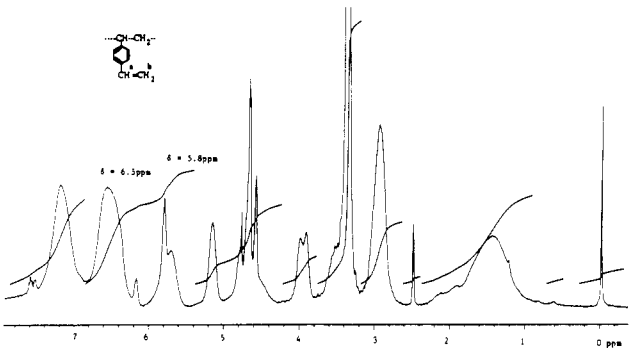

Figure 1. ^{1}H NMR of the P(DMEVBAC-VS) in DMSO-*d*.

P(DMEVBAC-VS//P (hydrophilic)//P (hydrophobic)) Polymer). The Wittig reaction converts P(DMEVBAC-TPVBPC) into the copolymer P(DMEVBAC-VS) (Scheme I). The ^{1}H NMR of P(DMEVBAC-VS) dissolved in DMSO-*d* indicates the presence of vinylstyrene (VS) units on the polymer chain, since the peaks at 5.8 and 6.5 ppm (Figure 1) correspond to the resonance absorptions of the hydrogen atoms of the vinyl groups. Because an excess amount of formaldehyde was used in the reaction, the Wittig reaction can be considered to be quantitative. This was verified by determining the amount of triphenylphosphine oxide generated during the Wittig reaction. Consequently, the number of VS units is equal to the number of TPVBPC units in P(DMEVBAC-TPVBPC). The amounts of P(DMEVBAC-VS) in various systems are listed in Table II.

In the next step, Span-80 molecules as well as the hydrophilic monomer and the initiator K_2SO_8 were introduced into the system which contains approximately 0.9–1.3 mmol of VS units. Since Span-80 is insoluble in water, some of its molecules are probably adsorbed on some of the VS units. When the system was polymerized by heating at 40–45 °C, the hydrophilic species reacted with some of the vinyl groups and hydrophilic polymer chains were grafted to the polymer backbone of P(DMEVBAC-VS). Indeed, the elemental analysis of nitrogen in the final product indicates the presence of acrylamide units (Table II). The poly(acrylamide) chains must be attached to the initial copolymer backbone since only in this manner can they become insoluble in water. As noted later in the paper, the final product is insoluble in both water and organic solvents. FT-IR and DSC investigations presented below also confirm the presence of grafted poly(acrylamide) side chains in the final polymer.

Table II
Various P(DMEVBAC-VS//PAM//PS) Polymers and the Amounts of Hydrophilic and Hydrophobic Grafted Polymers They Contain

entry	P(DMEVBAC-VS)[a] DMEVBAC (mmol/g of polymer)/ VS (mmol/g of polymer)	amt in the feedstock for polymerization P(DMEVBAC-VS) (g)	AM (mmol)	ST (mmol)	elemental anal. of AM units in the polymer (mmol/g)	ST units in[b] the polymer (mmol/g)
1	converted from P_1 2.2/3.5	0.36	25	25	3.16	7
2	converted from P_2 2.7/2.6	0.44	25	25	3.60	6
3	converted from P_3 3.2/1.85	0.52	12.5	25	2.29	7
4	as above	as above	25	25	3.43	6
5	as above	as above	38	25	4.64	5

[a] 20 mL of an aqueous solution of polymer converted via the Wittig reaction from the water-soluble polymers P_1, P_2, and P_3 (see Table I), respectively, was employed. [b] Calculated by subtracting the amounts of AM and P(DMEVBAC-VS) per gram of polymer.

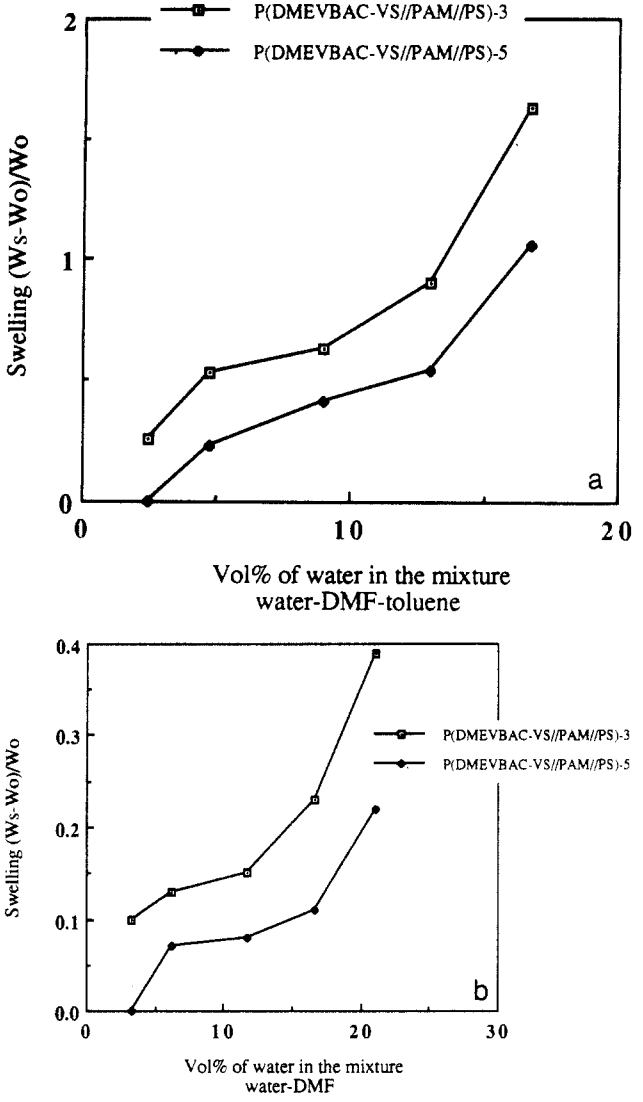

Figure 2. (a) Swelling of P(DMEVBAC-VS//PAM//PS) polymers in water–DMF–toluene (DMF/toluene = 3/1 volume ratio). (b) Swelling of the polymer in water–DMF. The numbers 3 and 5 refer to the corresponding entries in Table II.

Finally, the hydrophobic monomer was introduced together with AIBN into the polymerized system. Since Span-80 molecules are soluble into the hydrophobic monomer, a water-in-oil (w/o) concentrated emulsion is probably formed, in which the hydrophobic monomer constitutes the continuous phase and the aqueous phase the dispersed phase, with a volume fraction of about 0.9. The adsorption of Span-80 molecules on the interface between the continuous and dispersed phases and a high viscosity of the dispersed phase ensure the stability of the concentrated emulsion. The hydrophobic monomer reacts with the available VS units and hydrophobic polymer chains become grafted to the initial polymer backbone. The FT-IR and DSC investigations presented below indicate the presence of polystyrene in the final polymer. The polystyrene must be attached to the initial copolymer backbone because only in this way can it become insoluble in toluene or chloroform. The compositions of various P(DMEVABC-VS//PAM//PS) polymers are listed in Table II; the changes in the amount of the hydrophilic component (AM) have been made by increasing the amount of acrylamide in the feedstock.

For comparison purposes, polymer composites of PS and PAM were prepared by the polymerization of concentrated emulsions of aqueous solutions of acrylamide and K_2SO_8 in small amounts of styrene containing Span-80 and AIBN. When this composite material was placed

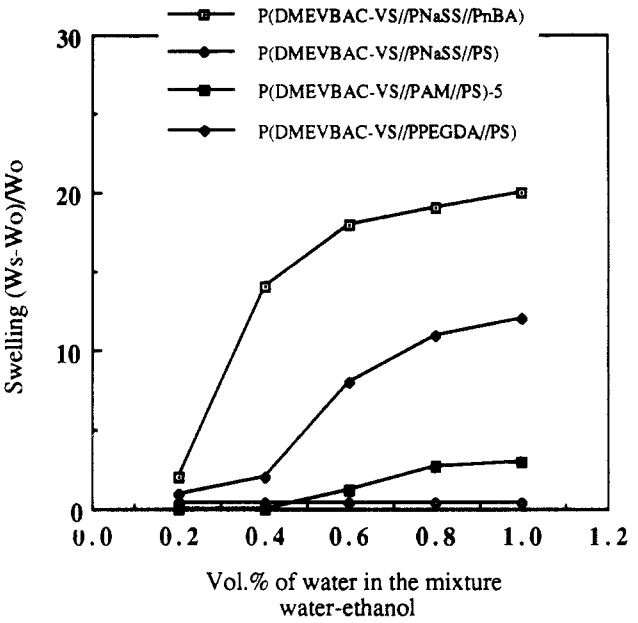

Figure 3. Swelling of the polymers in mixtures of water and ethanol. With the exception of the polymer P(DMEVBAC-VS//PAM//PS) which corresponds to entry 5 in Table II, the polymers are described in Table III.

in chloroform or water, the polystyrene or poly(acrylamide) dissolved, respectively. In contrast, P(DMEVBAC-VS//PAM//PS) does not dissolve either in water or in chloroform.

Swelling Tests. We found that the final polymer swells little in toluene or chloroform, which are good solvents for the grafted PS or P*n*BA, and while it does not dissolve, it swells considerably in water (because of its sufficiently high hydrophilicity). The swelling of P(DMEVBAC-VS//PAM//PS) (polymers 3 and 5 of Table II) in the water–DMF–toluene and water–DMF mixtures was also measured. DMF is a nonsolvent for PAM but has a moderate affinity for PS, while water is a good solvent for PAM, and toluene is for PS. The results (Figure 2a,b) show that (1) the swelling in both mixtures of the polymer containing a lower amount of PAM (polymer 3, Table II) is larger than that of the polymer containing a greater amount (polymer 5, Table II), (2) both polymers have higher swelling in the former than in the latter mixture, and (3) the swelling of both polymers increases with increasing volume percentage of water in the mixtures. From these observations and the fact that the final polymer swells little in toluene, one can conclude that the swelling of PAM in water triggers swelling of the PS side chains in DMF and particularly in the toluene and DMF mixture. The swelling of P(DMEVBAC-VS//PNaSS//PS), P(DMEVBAC-VS//PNaSS//P*n*BA), P(DMEVBAC-VS//PAM//PS), and P(DMEVBAC-VS//PPEGDA//PS) in various mixtures of water and ethanol is plotted in Figure 3.

Structural Characterization of the Hydrophilic and Hydrophobic Polymers. Five polymers containing hydrophilic and hydrophobic polymeric side chains have been prepared using the present methodology (Tables II and III). The FT-IR spectra of these polymers are given in Figure 4a,b, and the relevant absorptions of the characteristic functional groups are listed in Table III. The FT-IR spectrum of P(DMEVBAC-VS//PNaSS//PS) has a strong absorption band at 1184 cm^{-1} and a relatively weak absorption band at 833 cm^{-1}, which can be assigned to the stretching frequency of the sulfonate group and the out-of-plane bending frequency of the 1,4-disubstituted phenyl ring, respectively, and are therefore characteristic of the hydrophilic PNaSS side chains. The spectrum has

Table III
Elemental Analysis and FT-IR Fingerprints of the Polymers with Hydrophilic and Hydrophobic Polymeric Side Chains[a]

grafted polymers	AM (mg/g of polymer)	PEGDA (mg[b]/g of polymer)	NaSS (mg/g of polymer)	infrared characteristic adsorption bands (cm^{-1})
P(DMEVBAC-VS//PNaSS//PS)			445	1658 (benzene ring), 1184 ($-SO_3Na$)
P(DMEVBAC-VS//PPEGDA//PS)		576		1730 (C=O), 1601 (benzene ring), 1450 ($-CH_2-$), 1111 ($-CH_2OCH_2-$)
P(DMEVBAC-VS//PNaSS//P*n*BA)			488	1732 (C=O), 1654 (benzene ring), 1198 ($-SO_3Na$)
P(DMEVBAC-VS//PAM//P*n*BA)	275			3233 ($-NH_2$), 1733 (C=O), 1655 ($-CONH_2$), 1250, 1164 (-OR)

[a] Starting from the water-soluble polymer P_2 of Table I. [b] Calculated by assuming that the two ends of the PEG (MW = 400) molecule have been substituted by acryloyl groups.

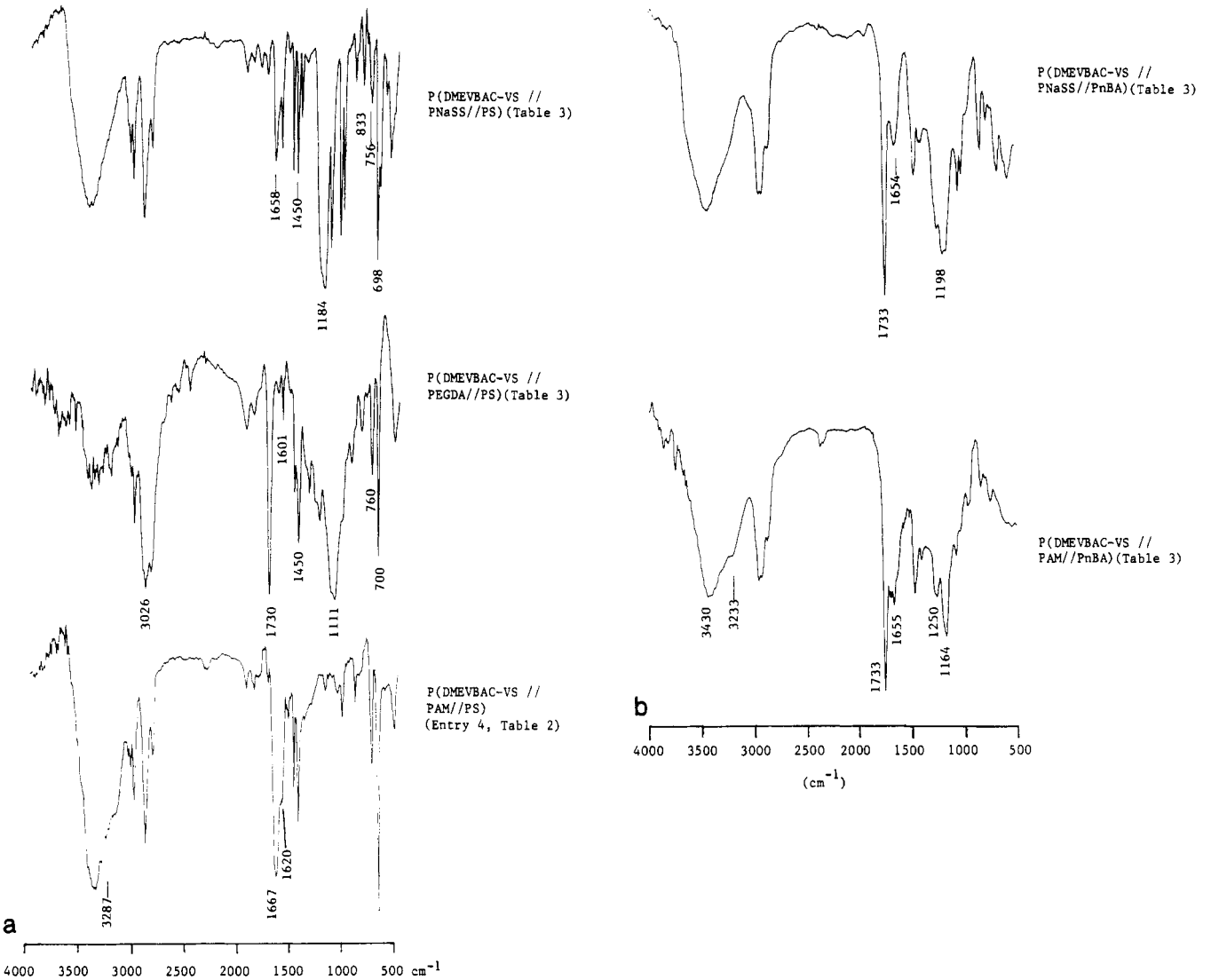

Figure 4. (a) FT-IR absorption spectra of the polystyrene side chain containing polymers. (b) FT-IR absorption spectra of the poly(butyl acrylate) side chain containing polymers.

also two absorption bands (698,756 cm^{-1}) which can be assigned to the out-of-plane bending frequencies of the monosubstituted phenyl ring and are therefore characteristic of the hydrophobic PS side chains. The FT-IR spectrum of P(DMEVBAC-VS//PPEGDA//PS) has a strong absorption band at 1111 cm^{-1}, which can be assigned to the unsymmetric stretching frequency of the ether, as well as an absorption band at 1730 cm^{-1} that can be assigned to the stretching frequency of the C=O bond of the terminal ester group. Both these groups are characteristic of the hydrophilic PPEGDA side chains. In addition, absorption bands (3026, 1601, 760, and 700 cm^{-1}) which are characteristic of the PS side chains are also observed. Similar comments can be made regarding the other three polymers.

The SEM micrograph (Figure 5a) of the P(DMEVBAC-VS//PNaSS//PS) polymer reveals a homogeneous texture, and the EDS surface elemental analysis carried out in various spots of about 1-μm size (Figure 5b) have not detected changes in composition. This indicates that the prepared polymer has a homogeneous structure at this length scale.

Thermal Analysis

The thermal properties of polystyrene,[10] poly(*n*-butyl acrylate),[11] and poly(acrylamide)[12] have been widely studied. Their glass transition temperatures T_g are 373 K for polystyrene, 218 K for poly(*n*-butyl acrylate), and 438 K for poly(acrylamide). The thermal properties of the polymers prepared by us have been investigated by

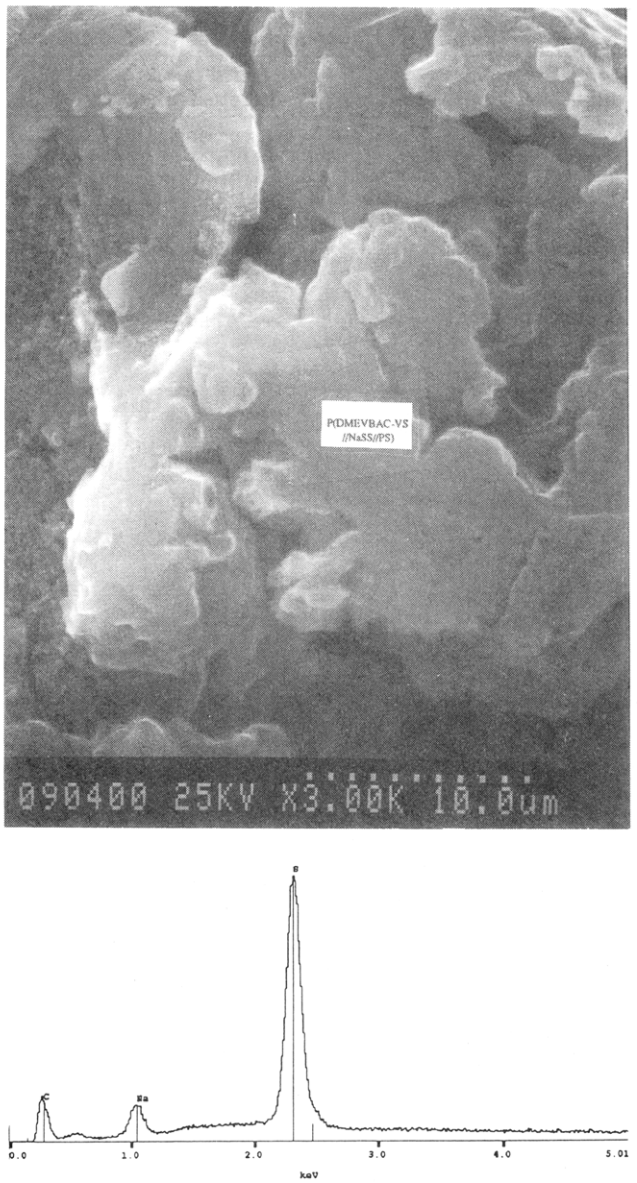

Figure 5. (a) Scanning electron micrograph of P(DMEVBAC–VS//PNaSS//PS). (b) Microarea elemental analysis for the specimen in (a).

DSC, and the results are presented in Figure 6. The temperature scanning curve of P(DMEVBAC–VS//PNaSS//PS) exhibits endothermal transitions at 374 and 429 K. The former represents the T_g of PS, and the latter, that of PNaSS. In the DSC curve of P(DMEVBAC–VS//PAM//PS), the T_g of PS increases to 410 K, probably because of the interactions between the PS and PAM side chains. The peak that appears at 443 K represents the T_g of PAM. On the DSC curve of the P(DMEVBAC–VS//PPEGDA//PS) polymer, the slope of the curve changes at both 453 and 535 K. Since the PPEGDA chains contain flexible PEG blocks, the continuous increase of the heat content of the polymers caused by the thermal motions of these blocks masks the T_g transition of PS which can no longer be detected. The temperature of 453 K probably represents the melting point of PPEGDA, and the temperature of 535 K represents the start of the decomposition of the comb polymer. As concerns the DSC curves of the P(DMEVBAC–VS//PNaSS//P*n*BA) and P(DMEVBAC–VS//PAM//P*n*BA) polymers, the temperatures of 354 and 340 K can be assigned to the melting point of P*n*BA in the above two polymers. The peak at 463 K on the DSC curve of the former polymer represents the T_g of PNaSS, which is higher than that of PNaSS in

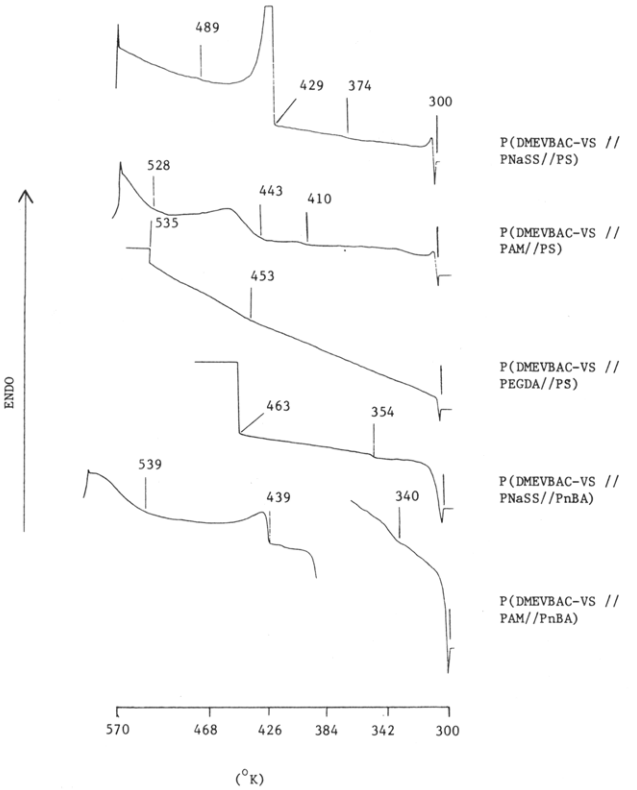

Figure 6. DSC curves for five prepared polymers.

P(DMEVBAC–VS//PNaSS//PS) probably because of the interactions among the pendant sodium sulfonate groups and carboxylate groups of the two kinds of side chains. The T_g of PAM in the latter polymer is near that of homopolyacrylamide.

The results of the thermal measurements show that the present comblike polymers exhibit two glass transition temperatures which are near those of the hydrophilic and hydrophobic side chains. This supports the contention that hydrophobic and hydrophilic chains are grafted to the P(DMEVBAC–VS) backbone.

Conclusions

Comblike polymers with hydrophobic and hydrophilic polymeric side chains can be synthesized by the methodology developed in this paper. The prepared polymers have been studied by performing solubility, swelling, DSC, and FT-IR measurements.

References and Notes

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