

Synthesis and Characterization of Anionic Graft Copolymers Containing Poly(Ethylene Oxide) Grafts

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ABSTRACT: Graft copolymers containing poly(ethylene oxide) side chain attached to maleic anhydride-*alt*-vinyl methyl ether (MA-VME) copolymer were prepared by coupling MA-VME and poly(ethylene glycol) monomethyl ether (MPEG) by esterification in DMF at 90°C. MPEG and dodecyl alcohol (DA) were grafted onto MA-VME copolymer in *o*-xylene at 140°C in the presence of *p*-toluene sulfonic acid as catalyst. The molecular weights of MPEG were found to influence the rate of the grafting reaction and the final degree of conversion. The graft copolymers were characterized by IR, GPC, and ¹H-NMR. DSC was used to examine thermal properties of the graft copolymers. The analysis

indicates that grafts have phase-separated morphology with the backbone and the MPEG grafts forming separate phases. The properties in aqueous solutions of these grafts were studied with respect to aggregation behavior and viscometric properties. In aqueous solution, the polymers exhibited polyelectrolyte behavior (i.e., a dramatic increase of the viscosity upon neutralization). Graft copolymers with DA have lower viscosities. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1138–1148, 2002

Key words: amphiphiles; graft copolymers; water-soluble polymers; surfactants; solution properties

INTRODUCTION

Amphiphilic block and graft copolymers are of considerable interest for various applications in which the combination of hydrophilic and hydrophobic properties of these materials may be utilized (e.g., as emulsifiers, dispersion stabilizers, and compatibilizers).^{1–5} The preparation and properties of amphiphilic grafts containing poly(ethylene oxide) (PEO) has been the subject of recent investigations.^{6–9} Their behavior in the solid phase and in solution is affected by interactions between the chemically dissimilar segments and their surroundings. The polymers form aggregates similar to micelles when they were dissolved in a good solvent for one block but poor solvent for the others.^{10,11} The micelle formation is driven by the phase separation of the hydrophobic blocks into a core, which is surrounded by a corona formed by lyophilic blocks swollen by the solvent. Amphiphilic block and grafts containing PEO may form mono- and polymolecular micellelike structures.

The objectives of our current investigation were to study the synthesis and properties of anionic grafts containing PEO and carboxylic groups attached to the

polymer backbone and to study their behavior in aqueous and salt solutions. The copolymers were prepared by grafting poly(ethylene glycol) monomethyl ether (MPEG) of different molecular weights and dodecyl alcohol (DA) onto maleic anhydride-*alt*-vinyl methyl ether (MA-VME) copolymer.

EXPERIMENTAL

Materials

A copolymer of MA-VME was obtained from Sigma-Aldrich GmbH (Germany). The molecular weight (M_n) was estimated at 63,000 according to gel permeation chromatography (GPC) in tetrahydrofuran (THF) at 25°C by using polystyrene (Polysciences) as standard. MPEG of different molecular weights (2000, 550, and 350 g/mol) (Sigma-Aldrich) and DA were used in the grafting reaction without purification. *p*-Toluene sulfonic acid monohydrate (pTs, Merck, p.a.) was used as catalyst. *o*-Xylene and dimethyl formamide (DMF) were used as the reaction medium. Methanol, THF, and cold diethyl ether were used as a solvent in the purification procedure. All solvents were obtained from Sigma-Aldrich and used as received.

Grafting of MPEG onto MA-VME copolymer

The backbone polymer MA-VME was dissolved in DMF and introduced into a glass flask. MPEG was

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used in a 50% molar surplus relative to the number of reactive succinic anhydride groups in the polymer. The total concentration of the reactants is 20 wt % in DMF. The grafting reaction was allowed to proceed under stirring at 90°C under N₂. Samples were withdrawn regularly as the reaction proceeded. When no further progress of the grafting reaction could be detected, according to the infrared spectra, methanol was added after the reaction mixture cooled down to 60°C.

Grafting of MPEG and DA onto MA-VME copolymer

Based on the fact that all repeating units of MA alternate with VME, the grafting of DA and MPEG onto MA-VME copolymer will be completed after adding an equimolar ratio of DA and MPEG to 50% of the reactive anhydride groups in the polymer backbone. DA and MPEG were allowed to react with MA-VME under N₂ at 140°C in *o*-xylene in the presence of pTs. The reaction mixture was refluxed until the theoretical amount of water was driven out. Methanol was added in excess after the reaction was finished to esterify residual acid groups.

Purification of graft copolymer

The crude products, after removal of *o*-xylene and DMF, were first precipitated from cold diethyl ether. The wet precipitate was immediately dissolved in THF and then diluted with aqueous 0.1M KOH. The THF was allowed to evaporate at room temperature. Nonreacted MPEG was removed from the solutions through dialysis membrane in water for 2 weeks (with a cut-off value of 600–800 and with cut-off 12,000–14,000 for removing MPEG2000). The purity of the grafts was analyzed by GPC by using distilled water as the eluant.

Characterization of graft copolymers

The conversion of anhydride groups in the polymer backbone to carboxylic acid and ester groups was achieved as followed by a Bruker FTIR spectrometer model IFS66 to evaluate the extent of grafting as a function of time. For this purpose, a few drops of the hot reaction mixture were put onto a KBr disc.

The compositions and structures of the grafts were determined by a Bruker 250-MHz ¹H-NMR type AC 250-F by using d₆-DMSO as a solvent at ambient temperature and tetramethylsilane as an internal standard. The MPEG and DA content in the grafts were calculated from ¹H-NMR spectra.

GPC analyses were run in THF on two Waters Ultrastaygel linear columns and in water on two Waters Ultrahydrogel linear column by using a refractive in-

dex (RI) detector. The flow rates were 1.0 and 0.2 mL/min, respectively. Polystyrene standards were used for molecular weight calibration in THF.

Differentials scanning calorimetric (DSC) thermograms were recorded on a Mettler DSC 30 equipped with a low-temperature cell. The samples were heated to 300°C, cooled down to –100°C, and reheated to 300°C. Heating and cooling rates were 10 K/min for each sample. Glass transition temperature (T_g , midpoint of the heat capacity change) and melting points (maximum endotherms) as well as heats of melting (ΔH_m) were evaluated from the second run.

Surface tension was determined at 25°C by the surface balance method by use of a Lecomte du Nouy tensiometer. Doubly distilled water ($\gamma = 72$ dyn/cm) was used for preparing the concentrated stock solutions of the graft copolymers. Several concentrations were prepared by diluting the stock solution with doubly distilled water to the appropriate concentration to be used in the determination of critical micelle concentration (CMC). The diluted solutions were allowed to stand for 24 h before the surface tension measurements.

Different solutions of grafts having 2 wt % of the polymer in both double-distilled water and saline solutions (1–5 wt % KCl) were prepared. Each solution was heated with stirring until it became turbid. Upon cooling, the turbidity started to disappear. The temperature at which the solution became completely clear was recorded as the cloud point of this particular solution.

Static light scattering (SLS) measurements were performed on a modified static light scattering apparatus FICA 50 (SLS Systemtechnik G. Baur, Freiburg, Germany) by using a laser light source (633 nm) at scattering angles $15^\circ \leq \theta \leq 145^\circ$ in steps of 5°.

Measurements for all prepared grafts were carried out in the concentration range 0.5–6 mg/ml of aqueous and salt solutions (0.01 and 0.1M KCl) at 25°C. The solutions were filtered through a 0.2- μ m filter and allowed to adapt to room temperature before being transferred into the light scattering cell. The refractive index increment was measured by a DLS 1 (SLS Systemtechnik G. Baur).

Viscosity measurements were carried out at 25°C by using a Ubbelohde viscometer. Solutions containing 0.5–20 mg/ml of copolymers in water or KCl solution were neutralized with KOH to the desired pH. Before use, all stock solutions were filtered through a 0.45- μ m polytetrafluoroethylene (PTFE) membrane (Millipore). The errors in the viscosity measurements were <0.5%.

RESULTS AND DISCUSSION

The graft copolymers can be prepared by a variety of methods. In a previous communication,² graft copol-

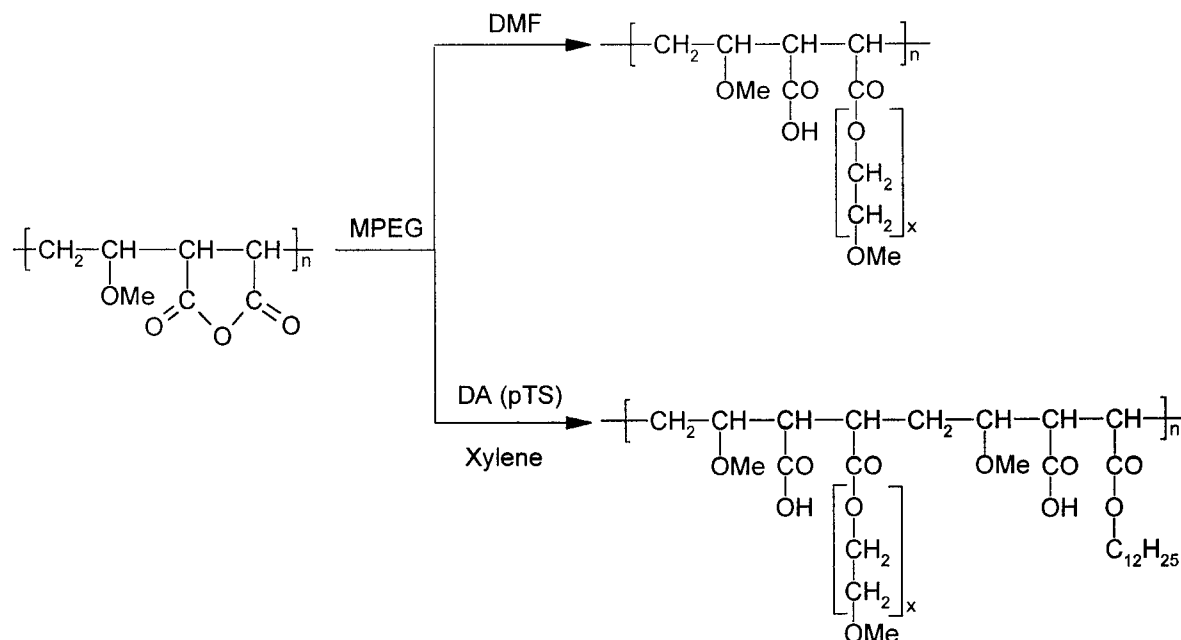


Figure 1 Reaction scheme for grafting of MA-VME copolymer with MPEG and DA.

ymers from polystyrene waste were prepared by the esterification of carboxylic side chain with poly(ethylene glycol) (PEG) of different molecular weights. In the present work, we utilized grafting by using the anhydride groups of MA-VME copolymer as reactive sites in reactions with MPEG of different molecular weights. The reaction scheme is shown in Figure 1.

The backbone MA-VME copolymer was grafted by MPEG in DMF solution without any catalyst. The grafting reaction involves a ring opening reaction between the hydroxyl end groups of MPEG and the anhydride units in the polymer backbone. Experimental data are collected in Table I.

Reactions between macromolecules are generally difficult to carry out because the other reactive groups often shield groups and complete conversions are generally not possible to reach. The reactivity of MPEG toward MA-VME copolymer was investigated for three different molecular weights of MPEG. The consumption of anhydride groups in the grafting reaction

of MA-VME copolymer with MPEG was determined by measuring the increase of the absorption peak of C=O stretching of ester group (IR analyses). The ester and carboxylic acid groups formed in the reaction have peaks at 1748 and 1680 cm^{-1} , respectively. The degree of conversion as well as the reaction rate seemed to be dependent on the length of the MPEG chains. It was observed that larger chain lengths of MPEG decrease the reaction rate. This finding is in agreement with the conclusion of the work carried out by Derand and Wesslen.¹² This may be explained on the basis of increased shielding of the backbone reaction sites at larger chain lengths of MPEG, because of changes in conformation as the reaction with MPEG proceeds.

By allowing the graft copolymers to react with an excess of methanol after the reaction with MPEG had ceased, it was shown that the complete conversion of the anhydride groups was possible to reach. The structures of the produced grafts were determined by using

TABLE I
Preparation and Composition of MA-VME Graft Copolymers with Polyethylene Glycol Monomethyl Ether Having Different Molecular Weights

Designation	M_n MPEG (g/mol)	Reaction time (h)	Conversion anhydride ^a (mol %)	MPEG in graft copolymer (wt %)	DA (%w/w)	$10^{-3} M_n^b$ (g/mol)
MA-VME350	350	48	7	25	—	93
MA-VME550	550	50	12	35	—	104
MA-VME2000	2000	72	20	65	—	195
MA-VME550/DA	550	4.5	18	28	5	135
MA-VME2000/DA	2000	9.5	28	56	8	181

^a Determined by ¹H-NMR.

^b Calculated from GPC of backbone and ¹H-NMR of the graft copolymer.

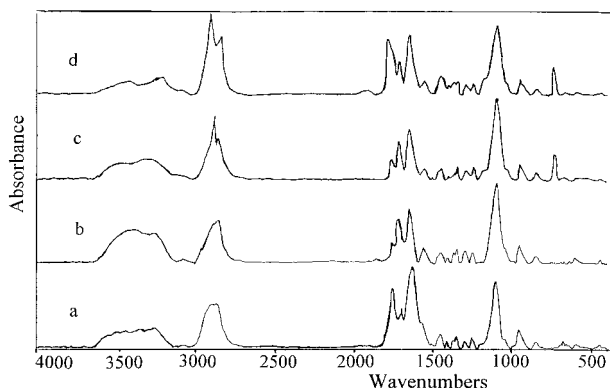


Figure 2 FTIR spectra of MA-VME grafted with MPEG: (a) MA-VME2000; (b) MA-VME350; and grafted with MPEG and DA: (c) MA-VME550/DA; (d) MA-VME2000/DA.

FTIR spectroscopy. The spectra of MA-VME grafts with MPEG were represented in Figure 2. It was observed that spectra of the all MPEG grafts are nearly identical. A representative infrared spectral pattern of MA-VME grafts with MPEG2000 and 350 are shown in Figure 2(a) and 2(b), respectively. The spectra of resulting polymer showed no absorption lines from anhydride groups of MA-VME copolymer, and thus, it was assumed that the reaction was complete. The carbonyl stretching at 1745 cm^{-1} , C=O of ester, peak at 1700 cm^{-1} , represents acid, and a significant ether peak at 1120 cm^{-1} indicates that MPEG were grafted onto the MA-VME copolymer.

The grafting of DA and MPEG onto MA-VME copolymer was completed in *o*-xylene in the presence of pTs as catalyst. This is because the true solution of both DA and MPEG with MA-VME was obtained in xylene above 100°C . The reaction conditions are listed in Table I. It was noted that the accessibility and reactivity of the functional groups might limit the esterification reaction rates. In the present case, the reactivity of the anhydride group toward MPEG is relatively low and consequently the reaction rates could be rather low. The low rate can be compensated by incorporation of a low molecular weight alcohol such as DA. The spectra of copolymers grafted with DA and MPEG550 and 2000 are recorded in Figure 2(c) and 2(d), respectively. The same manner observed in spectra of MA-VME grafts with MPEG is detected in grafts with DA and MPEG. The incorporation of DA in the grafts is shown by the presence of the strong bending vibration at 720 cm^{-1} representing the C—(CH₂)—C of the long alkyl DA moiety of the grafts.¹³ The listed values of the reaction time (Table I) indicate that the conversion of MA was completed in xylene within a shorter time than that detected in DMF. This may be attributed to the reaction of MA-VME copolymer with low molecular weight alcohol (DA) increasing the compatibility of esterified copolymer with MPEG. The increase in compatibility leads

to enhancement of the probability of completing the chemical reaction between both MPEG and MA-VME copolymer.

Further confirmation for the structure of MA-VME grafts with both DA and MPEG was obtained by ¹H-NMR spectroscopy. The NMR spectral shifts (σ) of MA-VME copolymer and its grafts with MPEG2000, 350, and 550/DA were selected to illustrate the structure of the grafted copolymers (Fig. 3). The protons of oxyethylene units at $\sigma = 3.56\text{ ppm}$, —OCH₃ protons of PEG at $\sigma = 3.22\text{ ppm}$, —OCH₃ protons of VME at $\sigma = 3.41\text{ ppm}$, and the methylene protons in polymer backbone at $\sigma = 1.8\text{ ppm}$ are observed in the spectra of all grafts. The new peaks at $\sigma = 4.25, 1.3,$ and 0.88 ppm are assigned for —OCH₂—, —(CH₂)₁₀, and —CH₃ of esterified DA grafts, respectively.¹⁴ ¹H-NMR spectroscopic analysis was used for determining the chemical composition for graft or block copolymers through integration of the characteristic signal.² Accordingly, the same procedure was applied through this work for determining the grafting percentage of the synthesized grafts. In this respect, the composition analysis is based on two signals, namely, at 3.22 ppm (assigned to —OCH₃ protons of PEG) and at 3.41 ppm (assigned to —OCH₃ protons of VME). The ratio of the integrals of these two signals is utilized for determining the percentage of grafting, which is expressed as the percentage of MPEG. The MPEG contents in the grafts were determined from ¹H-NMR and listed in Table I.

Solubility and surface activity of the grafts

The graft copolymers used in the present investigation were composed of main chains carrying pendant carboxylic groups and grafts consisting of MPEG. A minor fraction of the anhydride groups were utilized in the grafting reaction, which left a number of anhydride groups available for hydrolysis reaction. The latter reaction gives a main chain containing a large number of carboxylic acid groups. The solubility and state of graft solutions should depend on the backbone composition, pH, ionization of carboxyl groups along the main chain, and hydrogen bonds between polar groups of grafts. Consequently, because of different types of interactions, the solution behaviors of the grafts are difficult to predict.

The solubility of the grafts depends on the method of purification. It was observed that gellike substances were rapidly formed when the grafts were isolated from DMF and xylene solutions by precipitation and drying. This gel cannot be dissolved in solvents even in acidic or alkaline solutions. However, if the polymers were neutralized with KOH before drying, they will remain completely soluble in water. This can be attributed to inter- and intramolecular hydrogen bonding between COOH and MPEG grafts and formation of interchain anhydride groups on drying.

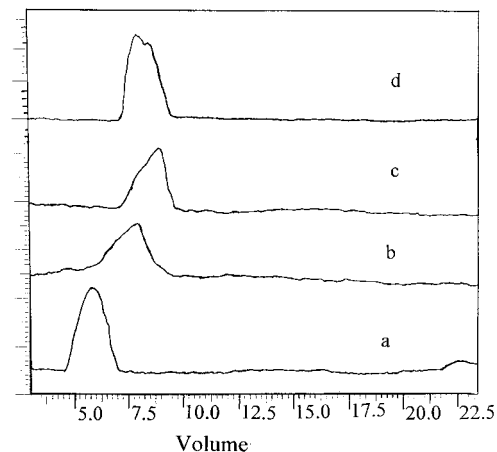
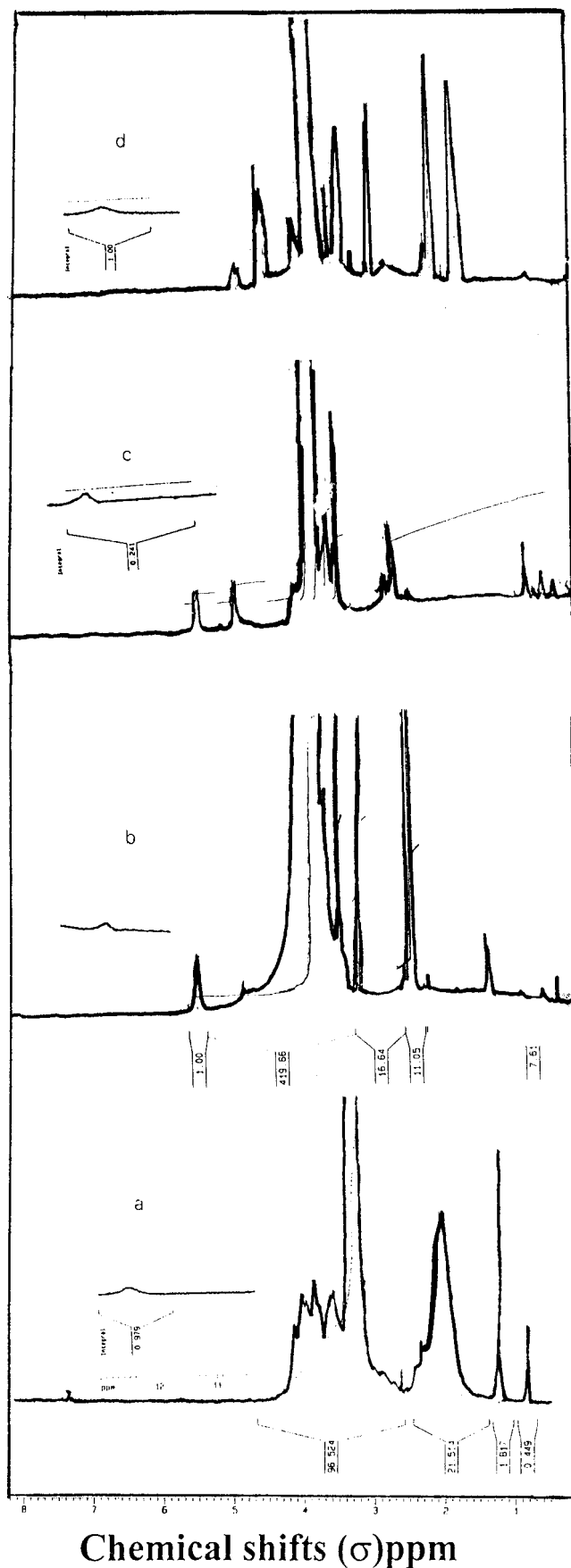


Figure 4 GPC elution curve in aqueous solutions of graft copolymers after dialysis. (a) MA-VME2000; (b) MA-VME550; (c) MA-VME350; (d) MA-VME2000/DA.

However, physically crosslinked gels usually can be reversed by changing the pH or the ionic strength.¹⁵

The graft copolymers were successfully purified by dialysis in aqueous solution. The purity of the products was confirmed by aqueous GPC, as shown in Figure 4. The samples eluate mainly at the void volume of GPC column. A similar behavior was reported for other types of amphiphilic PEG and MPEG graft copolymers and can be explained by aggregation or ion exclusion.^{15,16}

The graft copolymers were soluble in pure water as well as in KCl solution at low ionic strengths with no residues after 24 h. The solubility depends on the molecular weight as well as on the number of the hydrophilic MPEG branches that connected to the hydrophobic backbone. However, the different segments in the graft copolymers have dissimilar solubility properties. This difference in solubility is due to the difference in hydrophil-lipophil balance (HLB) of the grafts. The HLB values of the grafts were calculated according to the Davies formula.¹⁷ The equation of HLB is (HLP-7 = hydrophilic group number - lipophilic group number). The resulting (HLB-7) was dependent on the contributions of hydrophilic and lipophilic structural units present in the molecule. In the present system, PEO was added as hydrophilic and its value was calculated from the percentage of MPEG in the grafts (Table I). The HLB values were determined and listed in Table II. The data indicate that the HLB values increase with increasing percentage of MPEG in graft and with the molecular weight of the MPEG side chain.

Figure 3 ¹H-NMR spectra of graft copolymers in DMSO: (a) MA-VME copolymer; (b) MA-VME2000; (c) MA-VME350; (d) MA-VME550/DA.

TABLE II
Amphiphilic and Aggregation Behavior of Graft Copolymers in Aqueous and KCl Solutions
(A_2 in 10^{-6} ml mol/g²; $\langle s^2 \rangle^{1/2}$ in nm)

Designation	HLB	10^3 CMC at 35°C (mol dm ⁻³)	γ_{CMC} at 35°C (mN m ⁻¹)	SLS parameters						Cloud point ^a (°C)
				In water		0.01M KCl		0.1M KCl		
				A_2	$\langle s^2 \rangle^{1/2}$	A_2	$\langle s^2 \rangle^{1/2}$	A_2	$\langle s^2 \rangle^{1/2}$	
MA-VME350	30.5	0.073	29.00	194	88	-1.1	120	-2.9	129	60
MA-VME550	31.9	0.126	30.00	39.1	142	4.0	171	2.1	211	65
MA-VME2000	33.6	0.731	31.12	6.6	207	4.1	210	3.6	212	68
MA-VME 550/DA	22.1	0.063	29.00	-2.5	180	-5.3	185	-6.9	192	70
MA-VME 2000/DA	25.8	0.432	28.42	1.2	185	-0.4	195	-1.3	205	63

^a In 3 wt % NaCl.

The CMC of the water-soluble grafts were determined by the surface balance methods, in which the abrupt change in the slopes of γ versus the natural logarithm of concentration ($\ln C$) plots is taken as CMC. The obtained values at 25°C are listed in Table II together with the values of the surface tensions at CMC (γ_{CMC}) and cloud points. It is noted that the values of CMC decrease with an increase in the number of ethylene oxide content of MPEG in graft polymers and incorporation of DA as side chain. This may be attributed to the effect of the percentage of grafting on the conformation of these molecules. In previous articles,^{2,16-18} the effect of the alkyl group and the presence of carboxylic groups as a side chain of hydrophobe on surface activity for some grafts were studied. It has been noted that the presence of the carboxylic group will prevent the formation of a dense core due to its interaction with water and side chain of MPEG.

Hydrophobically modified polyelectrolytes are known to form interchain aggregates in aqueous solution. The efficiency of the aggregation process depends on the content and the nature of the hydrophobic groups and their distribution along the chain.¹⁷⁻¹⁹ In literature, the aggregation behavior was determined by SLS, quasi-elastic light scattering, flow field-flow fractionation, and transmission electron microscopy.¹⁸⁻²¹ In the present study, the aggregation behavior of the graft copolymers was studied by analyzing values of radius of gyration ($\langle s^2 \rangle^{1/2}$) and second virial coefficient (A_2), which was determined by SLS in aqueous, 0.01, and 0.1N KCl solutions (Table III). The values of A_2 for graft aqueous solutions are quite near to zero and decrease with decreasing molecular weight of MPEG and incorporation of DA as side chain. It was also noted that MPEG2000 grafts give a higher value of $\langle s^2 \rangle^{1/2}$ than other grafts. These results indicate that the grafts with MPEG2000 consist of a single polymer chain in aqueous solution, whereas the grafts with DA and lower molecular weight tend to form minor aggregates in aqueous solution. The conformation of these aggregates is not clear, but it seems to be reasonable to expect that the hydrophobic

groups of the macromolecule should accumulate at the center of the structure. A plausible model of these aggregates would be a micellelike structure where the hydrophobic parts of the backbone are oriented toward the interior of the structure and the hydrophilic MPEG grafts are oriented toward the aqueous phase. This rearrangement would minimize the exposure of the polymer backbone to the aqueous phase.²¹ This will reflect on the CMC value (Table II) for polymeric grafts when the molecular weight of MPEG decreases and introduces DA in grafts. On the other hand, the interaction of carboxylic acid groups in the grafts with MPEG grafts or with water would prevent the backbone from forming a dense core and leads to the increase in CMC values. It has been concluded that hydrophobically modified grafts with DA may form aggregates in aqueous solution. The solution properties of these anionic graft copolymers are similar to behaviors of grafts of maleic anhydride and styrene, methyl methacrylate, and ethylhexyl methacrylate with MPEG.²¹ Our discussion was based on the finding of solution properties observed by Derand et al.²¹

SLS measurements were also made in 0.01 and 0.1N KCl solution to study the effect of ionic strength on aggregation behavior. It was observed that negative values of A_2 and high $\langle s^2 \rangle$ for grafts with MPEG550, 350, and DA/2000 were recorded. This indicates that a dramatic shift toward polymer aggregates rather than single polymer chain is observed when the ionic strength is increased. The positive values of A_2 and

TABLE III
Thermal and Melting Characteristics
of Graft Copolymers

Designation	T_g (°C)	T_m (°C)		ΔH_m (J/g)
		MPEG	MA-VME	
MA-VME350	—	—	280	—
MA-VME550	—	—	285	—
MA-VME2000	—	45	290	40.9
MA-VME550/DA	95.6	—	270	—
MA-VME2000/DA	—	44.1	275	68.3

^a ΔH_m for pure MPEG2000: 80.4 J/g at $T_m = 53.4^\circ\text{C}$.

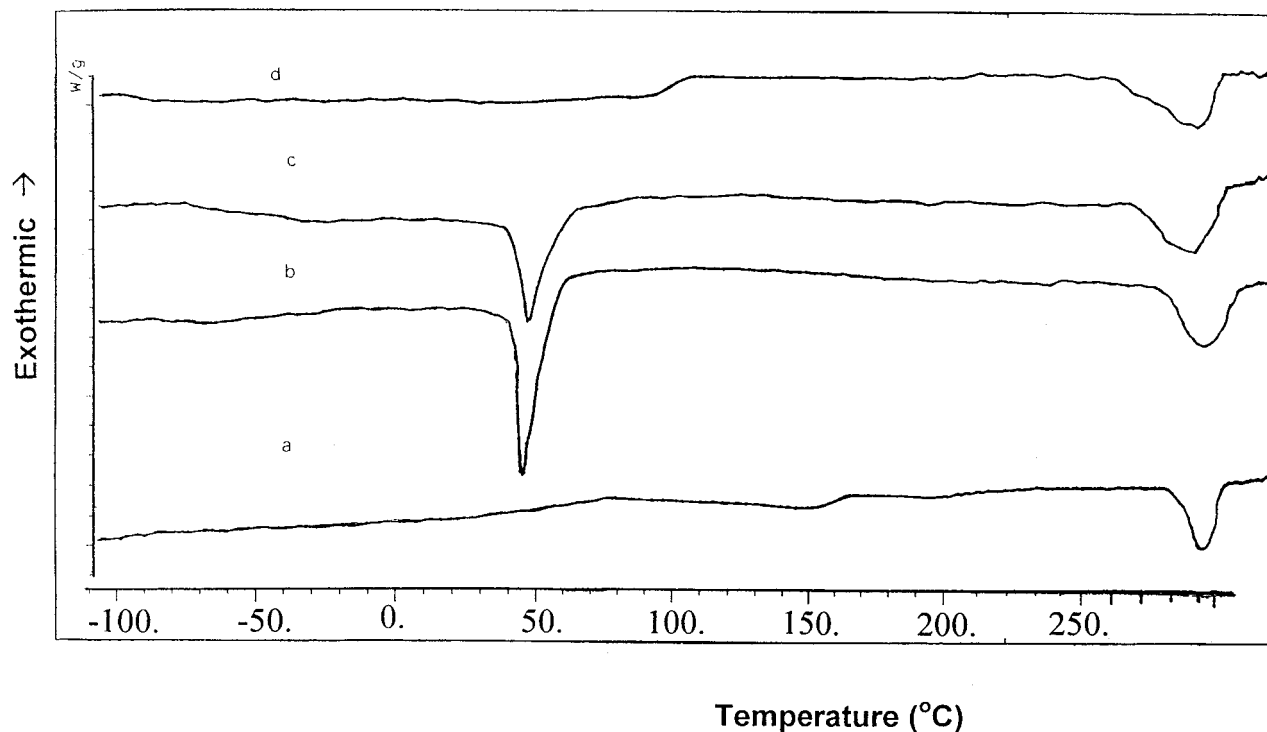


Figure 5 DSC traces of (a) MA-VME copolymer; (b) MA-VME2000; (c) MA-VME2000/DA; (d) MA-VME550/DA.

high $\langle s^2 \rangle^{1/2}$ of MPEG550 and MPEG2000 grafts in salt solutions indicate the minor aggregation tendency in salt solutions. It was also noticed that the relatively same value of A_2 for MPEG550 and MPEG2000 grafts in 0.1N KCl solution. This can be explained on the basis of the higher degree of hydrophobicity of MPEG550 seeming to induce an increase of aggrega-

tion than MPEG2000 grafts. Similar behavior is well known for block copolymers placed in a selective solvent.²²

The aggregation behavior of the graft copolymers can be explained by changes in the solubility of the backbone decreasing as the concentration of KCl increases. The ionic groups present along the backbone

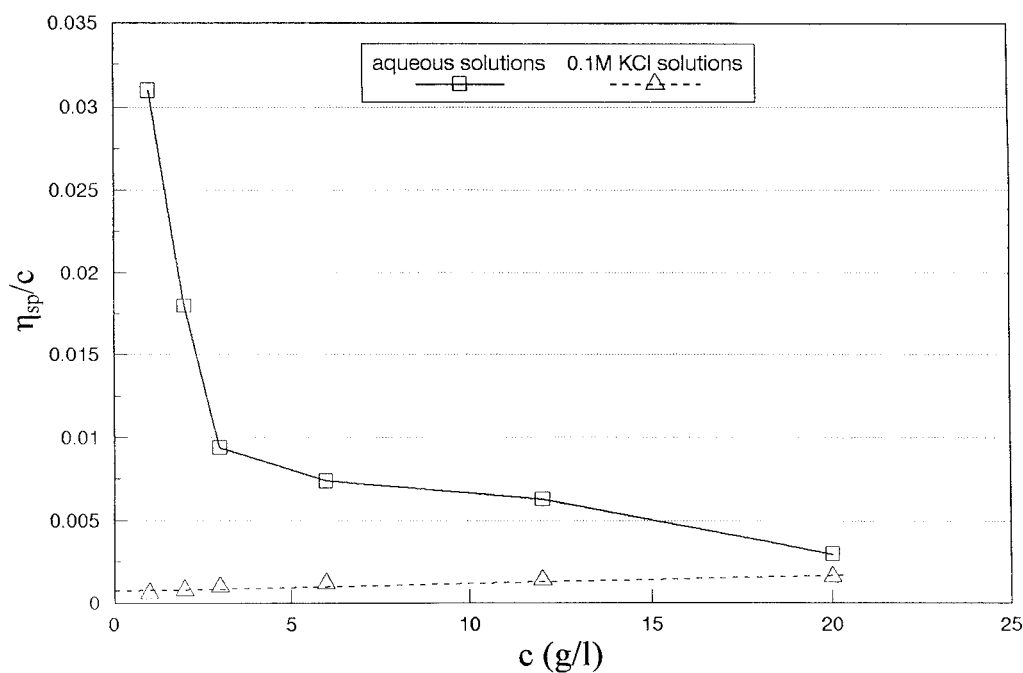


Figure 6 Concentration dependence of reduced viscosity (η_{sp}/c in L/g) of MA-VME2000 in aqueous solution and 0.1M KCl.

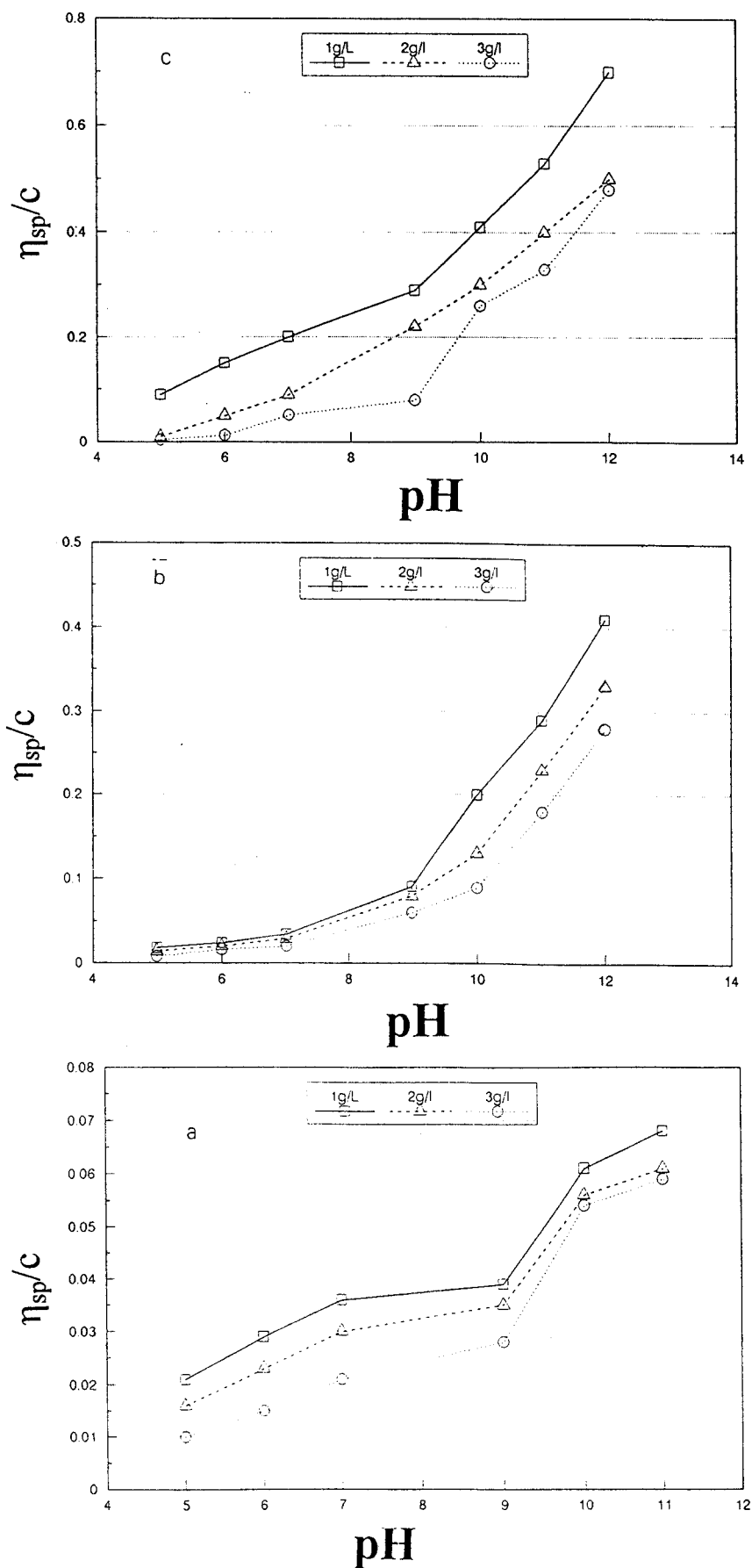


Figure 7 Reduced viscosity (η_{sp}/c in L/g) versus concentration dependence of pH to show neutralization: (a) MA-VME350; (b) MA-VME550; (c) MA-VME2000.

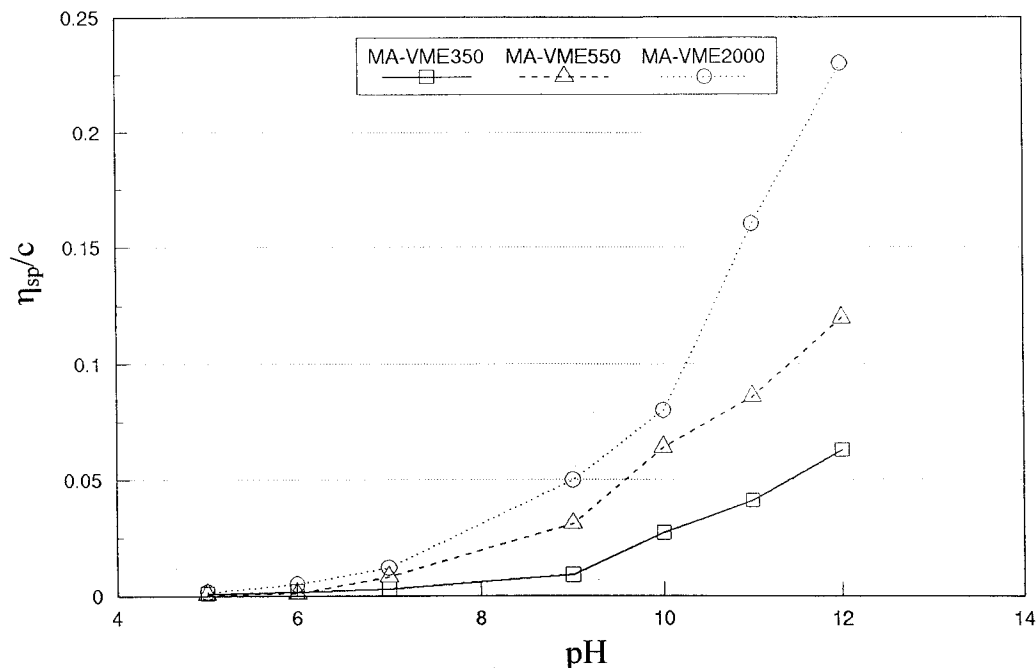


Figure 8 pH dependence of reduced viscosity (η_{sp}/c in L/g) of neutralized MA-VME2000 in 0.1M KCl.

will be screened by the salt and the electrostatic repulsion forces will be accordingly reduced. This effect will allow the hydrophobic groups to increasingly interact, which would lead to a more compact conformation of the main chain.

Thermal properties

DSC scans for MA-VME copolymer and its grafts with MPEG and DA are given in Figure 5. Values of T_g and T_m are listed in Table III. Because of the large difference in the polarity between the backbone and the MPEG grafts, a phase-separated morphology was obtained for MPEG grafts regardless of the chain length of MPEG grafts. The backbone polymer formed phase with a melting temperature of 270–290°C according to DSC analyses (Table III). The separate phase formed by MPEG grafts was found to be crystalline for MPEG2000 and MPEG2000/DA grafts. The grafts with MPEG550 and 350 cannot produce separate phases. This finding agrees with data obtained for different graft copolymers.^{21–23} In the DSC, traces show high sharp melting points for the copolymers with MPEG2000 and MPEG2000/DA, but no glass transitions could be detected. Only T_g of graft with MPEG550/DA could be detected. In this polymer, the backbone can be considered to be compatible with MPEG and DA grafts and due to internal plasticizing, T_g was lowered as compared to polymer backbone. This is despite the fact that hydrogen bonding and electrostatic interactions of the carboxylic acid groups formed in the ring-opening reaction tend to increase T_g of backbone.

Viscometric properties

Viscosity was measured for all grafts in pure water and 0.1M KCl solution. The reduced viscosity was plotted against the concentration of the graft polymer. In pure water, the viscosity increased as the concentration decreased. This fact contradicts the assumption that intermolecular association of the polymer is the cause of the viscosity increase. Differences in the charge distribution around the polymer main chain may be one reason for the observed effects. The previous behavior has been explained by an expansion of the polyelectrolyte chains caused by a decrease in ionic strength of the solution when the concentration of macromolecules is reduced for solutions containing charged macromolecules without added low molar mass salt. The extrapolation of η_{sp}/C to $C \rightarrow 0$ is not possible. Despite this, qualitative information can be obtained from the reduced viscosity at a constant polymer concentration. However, at high ionic strengths (i.e., in 0.1M KCl), a linear relationship between the reduced viscosity and the concentration of the grafts can be obtained. This behavior was observed for all grafts and MPEG2000 graft was selected as a representative (Fig. 6). The effect of degree of neutralization of the acid group by KOH is investigated by changing pH from 6 to 14.

The neutralization of MPEG2000, 550, and 350 grafts with KOH is shown in Figure 7(a–c). It was evident that the viscosity increased upon neutralizing the acid groups because of the extension of the graft copolymer. This can be attributed to the increase in neutralization causing a more rodlike structure of the polyelectrolyte.

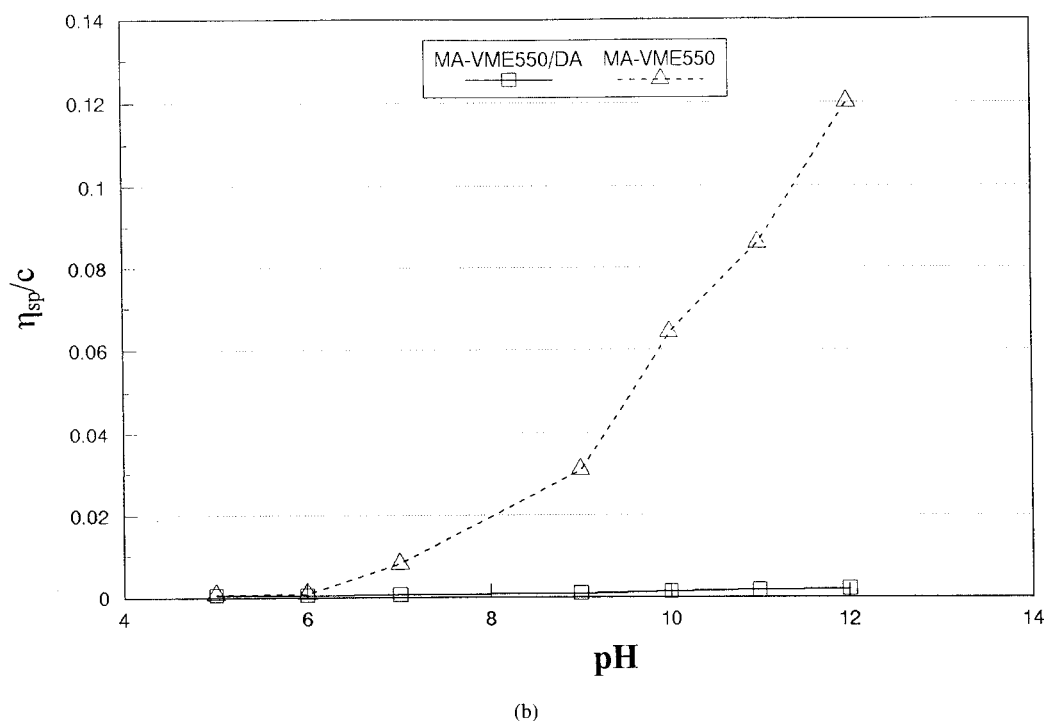
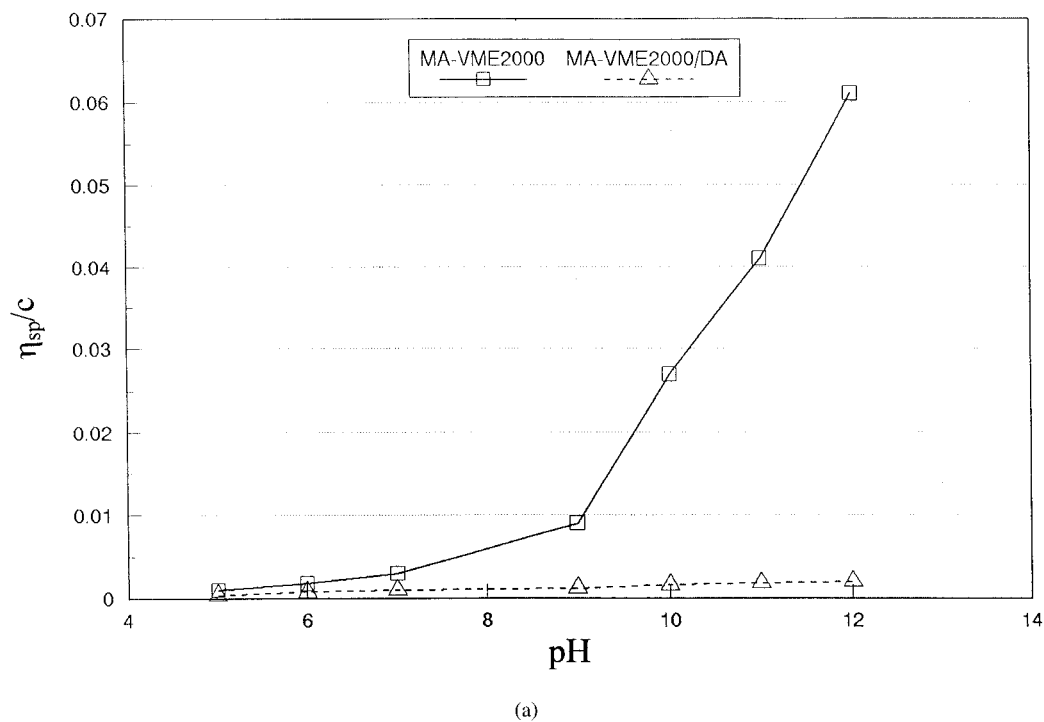


Figure 9 (a) pH dependence of reduced viscosity (η_{sp}/c in L/g) of neutralized MA-VME2000/DA and MA-MVE2000. (b) pH dependence of reduced viscosity (η_{sp}/c in L/g) of neutralized MA-VME550/DA and MA-VME550.

Figure 8 shows typical results for neutralization of MA-VME grafts in 0.1M KCl solutions. The relation between Figure 7 and 8 showed greatly different viscosity behaviors of different grafts, both in the absence and in the presence of KCl. For example, at the same weight concentration, a polymer having MPEG350 graft generally showed a higher viscosity than

MPEG2000 and 550 despite the fact that the latter grafts have a higher molecular weight. An explanation could be that the long MPEG grafts surrounding the backbone offer an environment richer in EO units than in the corresponding MPEG550 and 350 grafts and, consequently, a medium of different composition and dielectric constant. Counter ion salivation and charge

distribution may thus be quite different for the two different MPEG grafts.²¹

The incorporation of DA as side chain of backbone grafts and their effect on viscosity behavior upon neutralization was represented in Figure 9. These grafts behave differently and showed lower viscosity values. This can be attributed to intramolecular hydrophobic interactions and more compact conformations arise by the alkyl group. Similar results were reported from studies on solution viscosity of copolymer grafts.^{19,21,24}

CONCLUSION

The following conclusions can be drawn from the present investigation.

- Anionic grafts having different HLB can be synthesized through grafting MPEG and DA onto MA-VME copolymer.
- The incorporation of DA in grafts decreases reaction time.
- The molecular weight of the MPEG used in the grafting reaction influences both the reaction rate and the degree of conversion.
- SLS measurements indicate that the grafts in aqueous solution were mainly present as single molecules together with a minor fraction of aggregates. At increased ionic strengths, the medium caused aggregation of the hydrophobic segments of the backbone.
- Hydrophobically modified grafts with DA may form aggregates in aqueous solution.
- CMC values proved the formation of micellelike structures, in which the backbone forms a core that is surrounded by a corona consisting of hydrated MPEG grafts.
- DSC indicates the formation of separated phase morphology for MPEG2000 grafts with the backbone as well as the grafts forming crystalline phases.
- The reduced viscosity of grafts showed the typical behavior of a polyelectrolyte in aqueous solution. Graft copolymers having DA as a side chain were shown to need a minimum electrical charge to

overcome the intramolecular hydrophobic interaction.

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