

Synthesis and Characterization of Comb-Like Polymer PVC–Poly(Ethylene Oxide)

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ABSTRACT: A new series of amphiphilic graft-copolymers, composed of poly(vinyl chloride) (PVC) backbones and poly(ethylene oxide) side chains, was synthesized by chemical modification of PVC. The synthesis was based on the reaction between chlorine in PVC (polymerization degree 700) and sodium salt of polyethylene glycol (PEG). PEGs with molecular weights of 200 and 600 were used. The graft polymers were characterized by IR and gel permeation chromatography and the molecular parameters such as the average numbers of grafting chains on the PVC backbones were calculated as well as the grafting percent. The molecular weights of PEG were found to influence the rate of the grafting reaction and the final degree of conversion. The maximum grafting percentage of the resulted polymers after the purification was ca. 34%, regardless of the molecular weight of PEG. No gel was observed in the PVC-*g*-PEOs, in spite of the average numbers of grafting chains up to 32. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 475–479, 2000

Key words: amphiphilic graft copolymers; poly(ethylene glycol); chemical modification

INTRODUCTION

The synthesis and properties of amphiphilic graft copolymers with poly(ethylene oxide) grafts have been the interesting subject of recent investigations. For example, Wessle'n et al.¹ and Shinzo Yamashita et al.² have reported grafting of poly(ethylene oxide) (PEO) onto different polymer backbones such as acrylic copolymers and polystyrene copolymers. The particular properties of amphiphilic copolymers can be attributed to the incompatibility of the dissimilar segments in the polymers. They have interesting colloidal and interfacial behavior in solution³ as well as in the solid state⁴ and can be used for stabilization of

dispersions and emulsions, for stabilization of polymer blends,⁵ and for surface modification.^{6,7} In view of conductivity, PEO is a good solvent for alkali metal salts, and the solid solutions of, e.g., lithium salts, are used as polymer electrolytes in the solid batteries.⁸ In order to improve the ambient conductivity of PEO, some PEO block and graft copolymers were prepared.⁸ Our current investigation is aimed at the synthesis of amphiphilic graft copolymers with PEO side chains and poly(vinyl chloride) (PVC) backbones, which has well film-casting and plastic properties. In the successive articles we will report on the solution properties and the solid-state electrolytic behavior of the graft polymers.

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EXPERIMENTAL

Materials

PVC (XS-700) was supplied from Qilu Petroleum Chemical Industry Co. Ltd. (Shandong, China),

with a number-average molecular weight (M_{n1}) of 4.3722×10^4 . Polyethylene glycol (reagent grade) is the product of Shanghai Gaonan Chemical Plant (Shanghai, China); the molecular weights (M_{n2}), are 200 and 600, respectively, noted as PEG200, PEG600. The molecular weight distribution index, $M_w/M_n < 1.1$. Sodium, cyclohexanone, and methanol of commercial origins (reagent grade) were used without purification. Other solvents were all reagent grade and were used as commercially supplied.

Instruments

Gel permeation chromatography (GPC) analyses were run in THF at ambient temperature on NJ792 gel permeation chromatography meter with a silicone column. The flow rate was 1 mL/min. IR spectra were recorded for film samples casted from cyclohexanone solution onto KBr prisms using a Nicolet-5DX IR spectrometer.

Surface Tension Determination

Surface tension of graft polymer in cyclohexanone solution was determined at 25.5°C by the method of bubble pressure and were compared to that of PVC solution of cyclohexanone.

Synthesis of Polyethylene Glycol Sodium Solution

PEG (12 g, $[\text{OH}] = 4 \times 10^{-2}$ mol) was added to a 250-mL glass flask with 120 mL of cyclohexanone together, distilling out 20 mL of cyclohexanone. Metal sodium ($[\text{Na}] = 4 \times 10^{-3}$ mol) was introduced into the resulted mixtures, keeping the reaction under stirring at 150°C for 12 h.

Preparation of Graft Polymers

PVC was used in the grafting reaction without further purification. The reactions were carried out according to the following procedure. PVC backbone polymers (4.0 g, $[\text{Cl}] = 6.4 \times 10^{-2}$ mol) were added to a 250-mL glass flask with 120 mL of cyclohexanone. The mixture was heated until PVC was dissolved completely, distilling out 20 mL of cyclohexanone, and then 100 mL cyclohexanone solutions of polyethylene glycol sodium (PEGNa) prepared above were added dropwise to the resulted mixtures at desired temperature within 40 min, keeping the reaction under stirring at the same temperature for hours.

Isolation of the Graft Polymer

The gross polymer solution was a physical mixture of grafted PVC and PEG homopolymer as

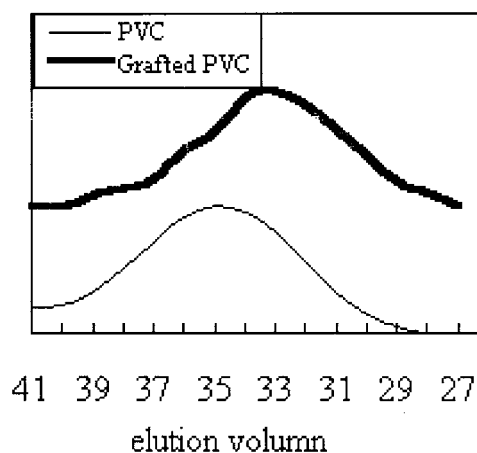


Figure 1 GPC analysis of PVC and PVC-g-PEG (sample 3) with THF eluent at ambient temperature.

well as solvent cyclohexanone. The isolation of graft copolymer was achieved by fractional precipitation technique using ethanol as a nonsolvent of grafted PVC. The amount of added ethanol was about equal to the volume of gross polymer solution. The precipitation of grafted PVC was filtered and washed with ethanol. The final product was extracted in a Soxhlet extractor with methanol for 48 h. The resulted polymer was dried in vacuum at 50°C for 3 h. The purity was analyzed by GPC using THF as solvent.

RESULTS AND DISCUSSION

Polymer Characterization

The formation of comb-like polymers was observed by IR spectroscopy and GPC with THF as eluent. Figure 1 represents the GPC curves of PVC and pure graft polymer and shows that the graft polymer sample has lower elution counts compared to that of PVC, thereby indicating the increase in the molecular weight. This increase is due to the presence of PEO side chains attached to the parent backbone polymer. IR spectrum of the graft polymer also confirms the presence of PEO side chains (Fig. 2). The characteristic peak of 1118 cm^{-1} from the IR spectrum of PVC-g-PEO (sample 3), which is attributed to the aliphatic C—O—C stretching vibration of the ether group, was detected as well as the typical peaks of PVC. From these analyses, the grafted structures of polymers were determined. The solution properties of the graft polymer that will be described below differ greatly from the parent backbone polymer,

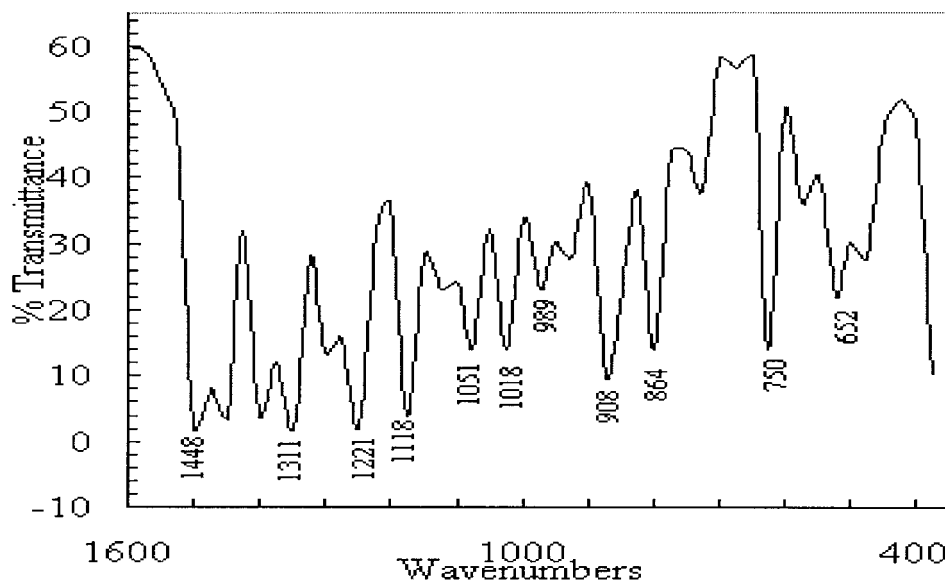


Figure 2 IR Spectrum of PVC-g-PEG (sample 3) recorded for film sample casted from cyclohexanone solution onto KBr prisms, using a Nicolet-5DX IR spectrometer.

providing further evidence of the formation of the grafted structures.

Molecular Parameters and Graft Conditions

Table I indicates the effect of variation of time and temperature on the grafting reactions of

PEGNa to PVC. The data of molecular parameters of the resulted polymers are also given in Table I.

Determining molecular parameters of grafted polymers is difficult, especially for the polymerization of monomer M, starting from sites created

Table I Synthesis of PVC-g-PEG Polymers

Sample No.	PVC (g)	PEG			Grafting Reaction		Chlorine (wt %)	PEG Content (%)	Molecular Parameter	
		M_n	Wt (g)	Na (g)	Temp (°C)	Time (h)			P_A (%)	N_g
1	4	600	12	0.12	130	2	51.4	9.1	1.0	7
2	4	600	12	0.12	130	5	44.9	20.0	2.6	18
3	4	600	12	0.12	130	10	40.5	27.5	3.9	27
4	4	600	12	0.12	150	2	41.5	25.8	3.6	25
5	4	600	12	0.12	150	1	44.8	20.1	2.6	18
6	4	600	12	0.12	110	10	48.4	14.2	1.7	12
7	4	600	12	0.10	110	15	46.8	16.8	2.1	14
8	4	600	12	0.10	110	5	50.2	11.1	1.3	9
9	4	600	12	0.10	130	7.5	41.9	25.2	3.4	24
10	4	200	4	0.11	140	2	51.2	8.6	2.9	20
11	4	200	4	0.11	140	3	50.6	9.6	3.3	23
12	4	200	4	0.11	140	5	48.2	13.3	4.7	33
13	4	200	4	0.10	130	5	50.3	10.0	3.4	24
14	4	200	4	0.10	130	2	52.8	6.2	2.1	14
15	4	200	4	0.10	130	10	49.4	11.4	3.9	27
16	4	200	4	0.10	120	10	49.7	11.0	3.9	27
17	4	200	4	0.10	120	5	51.9	7.5	2.5	17
18	4	200	4	0.10	120	15	48.8	12.3	4.3	30

P_A , the degree of grafting reaction; N_g , the average numbers of grafting chains.

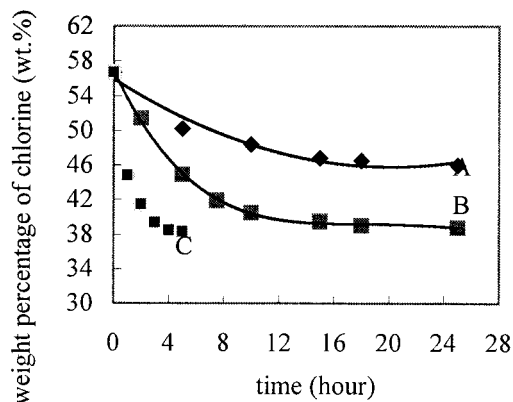


Figure 3 Weight percentage of chlorine (wt %) versus PVC and PEG600 grafting reaction time in different temperature. (A) 110°C; (B) 130°C; (C) 150°C.

on the backbone polymer. In the case of our investigation, because backbone polymer and grafted chains can be characterized independently, the well-defined polymers may be obtained. However, molecular parameters, such as the average numbers of grafting chains, are not well determined. In our previous articles,^{9,10} we reported the statistic method for the estimation of such structure parameters. Here the treatments for PEG grafting to PVC are represented. The formulas used were as follows:

$$W_{cl} = M_{cl}(1 - P_A) \times 100 / [M_1(1 - P_A) + P_A(M_{n_2} + M_{n_1} - 1)] \quad (1)$$

$$N_g = P_A \times P_{n_1} \quad (2)$$

where W_{cl} is the weight percentage of chlorine in the grafted polymers; M_{cl} is the atomic weight of chlorine; M_1 is the molecular weight of monomer unit of PVC; M_{n_1} is the molecular weight of ethylene unit; M_{n_2} is the molecular weight of PEG; P_A represents the degree of grafting reaction; P_{n_1} is the number average degree of polymerization of PVC; N_g is the average numbers of grafting chains.

From the formulas, grafting percent and PEG content can be determined as follows:

$$\text{Grafting percent} = \frac{\text{Wt of PEG grafted}}{\text{Wt of backbone polymer}} \times 100 \quad (3)$$

$$\text{PEG content} = \frac{\text{Wt of PEG grafted}}{\text{Wt of grafted polymer}} \times 100 \quad (4)$$

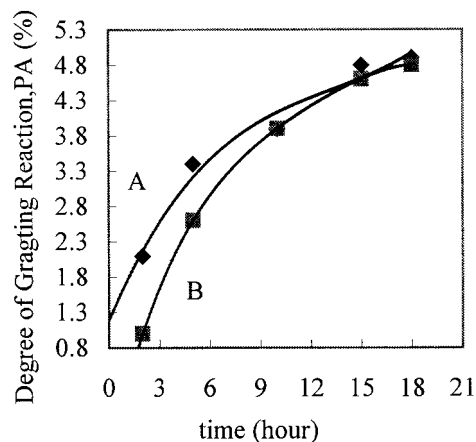


Figure 4 The degree of PVC grafting PEG reaction versus reaction time at 130°C. (A) PVC-g-PEG200; (B) PVC-g-PEG600.

It is demonstrated in this investigation that the reaction conditions play important roles in grafting of PEGNa onto PVC. The weight percentage of chlorine as a function of reaction time for various temperatures is shown in Figure 3. It can be seen that the weight percentage of chlorine decreases gradually with reaction time and tends to level, and high temperatures enhance the grafting reaction (wt % of Cl decreases faster with time). This result may be explained by assuming that the steric hindrance in the polymer-polymer reaction has depressed the grafting reaction, and the increase of temperature has somewhat overcome the steric hindrance according to the reference.²

Figures 4 and 5 show the relationship between the degree of grafting reaction (P_A), the average numbers of grafting chains (N_g), and the reaction time for different molecular weight of PEG at

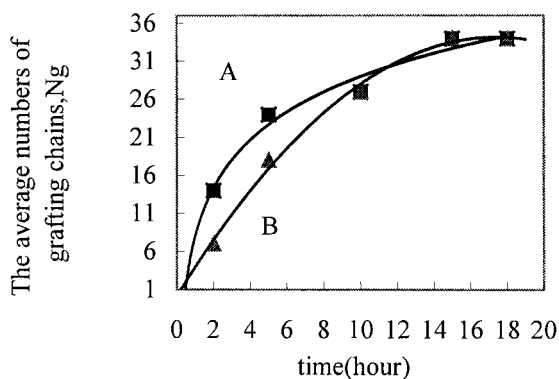


Figure 5 The average numbers of grafting chains of PVC-g-PEG copolymers relative to reaction time. (A) PVC-g-PEG200; (B) PVC-g-PEG600.

130°C. It is obvious that the smaller the PEG molecular weight, the larger the degree of grafting reaction as well as the average numbers of grafting chains. This indicates that the grafting reaction is controlled by diffusion. Although the reaction temperature is not low, the total concentration of polymers in the reaction system (ca. 8 g polymer/100 mL solvent) is high. No gel was observed in the PVC-*g*-PEOs, in spite of the average numbers of grafting chains up to 32, possibly due to the lower concentration of PEGNa in the solution.

Solution Properties of PVC-*g*-PEG

The characteristic properties of amphiphilic polymers represent in their varying conformations in solutions or in interfaces. The solution properties of amphiphilic polymers are determined by the length of side chains and the copolymer composition as well as solvents used. According to the solubility of backbone polymers and side chains in solution, the orientation of side chains will vary. If the solvent used favors the dissolving of backbone polymers, the grafted molecules will have such conformation that the side chains aggregate as a core surrounded by the backbone polymers, forming a shell solvated by the solvent medium, and the monomolecular "micelles," in which the backbone coils backward onto itself with the grafts inward, form. Otherwise the polymolecules will aggregate in such conformation that the core consists of backbone molecules and the shell of the grafts outward to the solvent. The graft polymers of PVC-*g*-PEG200 and -PEG600 resulted in the former structure in the solution of cyclohexanone.

Although PVC does not dissolve in water, the PVC solution of cyclohexanone showed a strong capacity to spread on the surface of water. It can rapidly spread on the surface, forming an approximately 71-cm² film for 0.04 ml of solution of 5% cyclohexanone. Grafted polymer solution of 5% cyclohexanone also demonstrated a strong capacity of spreading on the water surface, but in a different way. When it was dropped onto the surface of water, at first, it spread very little, only forming an approximately 2-cm² film for 0.04 mL of solution, dramatically drifting irregularly on the surface, similar to the way that metal sodium shows on the surface of water, and then more than 2 s later, the drifting film rapidly expanded, forming an approximately 44-cm² film. This result may be explained by assuming that there is a

kind of aggregated structure in the grafted polymer solution, and this kind of aggregated structure prevents the spreading film from becoming larger. Water molecules can destroy the aggregated structure, hydrolyzing the aggregated domain for example, making the aggregated domain collapse. The surface tension of grafted polymer solution of cyclohexanone is larger than that of the PVC solution of cyclohexanone from the bubble pressure method. This possibly indicates that hydrophilic side chains increase the energy of system, and the aggregated domain consists of hydrophilic PEG. PEG side chains aggregate as a core, avoiding contacting with the molecules of solvent in order to decrease the energy of system.

CONCLUSION

Poly(vinyl chloride) is a good starting material for the synthesis of graft polymers due to the presence of halogen atoms as reactive sites for branching. The molecular weight of PEG used influence the rate of the grafting reaction and the final degree of conversion. The maximum grafting percentage of the resulted polymers after the purification was ca. 34%, regardless of the molecular weight of PEG. No gel was observed in the PVC-*g*-PEOs, in spite of the average numbers of grafting chains up to 32.

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