

EFFECTS OF SOLVENT TREATMENT ON SURFACE MORPHOLOGY AND COMPOSITION OF POLY(METHYL METHACRYLATE)-*g*-POLY(ETHYLENE OXIDE)

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Abstract Surface morphology and composition of solution-cast films of poly(methyl methacrylate)-*g*-poly(ethylene oxide) (PMMA-*g*-PEO) were investigated by using XPS, DSC, SEM and contact angle measurement. The microphase separated structure of the copolymers was studied by TEM. Generally, for the same graft copolymer, the surface content of PEO or hydrophilicity can be as follows: Surface treated with petroleum ether or cyclohexane > surface untreated with solvent > surface treated with water or ethyl alcohol. Graft copolymer having longer PEO side chains and higher PEO content shows a separated PEO phase with even a certain degree of crystallinity on the surface. PEO crystallinity was destroyed by water or ethyl alcohol treatment; however, surface treatment with petroleum ether or cyclohexane favors the growth of PEO crystal. TEM shows that graft copolymers with longer PEO side chains (M_n of PEO, 3200) may readily undergo microphase separation and the shape and size of domains depend on the copolymer's composition.

Keywords PMMA-*g*-PEO, Surface morphology, Surface solvent treatment

INTRODUCTION

Polymeric materials have been widely used in both pharmaceutical and medical applications, and contributed significantly to the quality and effectiveness of the health care system. Since the surface layer of the polymers plays an important role in their practical application, therefore their surface properties have been the subject of increasing attention^[1–5]. Amphiphilic graft copolymers of PEO have received great attention as biomaterials. Interest in their applications, especially for modification of biomedical polymer surfaces and in the design of drug-delivery systems, has been rapidly growing^[6–10].

Amphiphilic graft copolymers having uniform PEO side chains and a definite structure can be used as a good model polymer for studying the relationship between surface properties and bulk structural parameters (such as bulk composition and PEO grafts), which can be obtained by copolymerization of hydrophobic vinyl monomers with PEO macromonomers. In a previous paper^[11], the surface characterization of PMMA-*g*-PEO prepared by using PEO macromonomer was investigated by XPS and contact-angle measurement. It was found that the surface properties of the PMMA-*g*-PEO copolymers were greatly influenced by their bulk PEO content and graft chain lengths, as well as surface contact media. The objective of the present investigation is to study the effect of solvent treatment on the surface morphology and composition of PMMA-*g*-PEO. Because PMMA homopolymers are amorphous and PEO homopolymers are semicrystalline, the amphiphilic PMMA-*g*-PEO copolymer consists of both amorphous and crystalline components. In addition, compared with excellent flexible PEO segments as side chains in the rubbery state, the mobility of PMMA segments as backbones in the glass state is much weaker. Thus, this should prove to be an interesting model system for understanding the environment sensitivity of the surface properties of multicomponent polymers.

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EXPERIMENTAL

Characterization of PMMA-g-PEO

PMMA-g-PEO copolymers were prepared using macromonomer technology^[11]. Their molecular characteristics are shown in Table 1. The molecular weights of PMMA-g-PEO and PEO macromonomers were respectively measured by gel permeation chromatography (GPC) and vapor phase osmometry (VPO) and the copolymer composition was determined by ¹H-NMR. ¹H-NMR spectra were recorded on a JEOL FX-90Ω spectrometer, using CDCl₃ or CD₃SOCD₃ as solvent and tetramethyl silane (TMS) as internal standard. The molar masses and molar mass distributions were investigated with a Knauer VPO apparatus, using toluene as solvent and bibenzoyl as standard, 37°C and a Waters-208 type apparatus, using tetrahydrofuran as eluent.

Table 1. Characteristics of PMMA-g-PEO*

Samples	A	B	C	D	E	F	G	H	I	J
$M_n \times 10^{-4}$	6.21	6.95	7.06	8.39	8.36	7.75	7.82	8.10	8.26	7.55
M_w/M_n	1.8	1.8	1.9	2.1	2.1	1.8	1.8	2.0	1.9	1.8
EO (mol%)	34.7	49.1	56.8	61.1	68.8	38.0	49.2	56.5	65.2	74.1
a/b	4.3	2.4	1.9	1.4	1.0	3.7	2.4	1.7	1.2	0.8

* M_n of PEO macromonomer in copolymer A, B, C, D or E is 1650; M_n of PEO macromonomer in the copolymer F, G, H, I or J is 3200; a/b is PMMA/PEO.

Preparation of Thin Polymer Film

Thin polymer films for XPS and contact-angle measurements were cast from dilute solution of PMMA-PEO in chloroform (1%) on clean glass plates. The obtained films were dried for three days in vacuum at ambient temperature. For each polymer sample, several replica films were prepared for XPS, DSC, SEM and contact-angle measurements.

Treatment with Solvents

Thin polymer films obtained by the above method were first immersed in different kinds of solvent (water, ethyl alcohol, cyclohexane or petroleum ether) for 10 h, and then dried for three days in vacuum at ambient temperature.

X-ray Photoelectron Spectroscopy (XPS)

Spectra were recorded on an ESCALAB MARK II spectrometer by using $Al_{K\alpha}$ exciting radiation. The basic pressure in the measurement chamber was kept around 1.33×10^{-6} Pa. The value of 285.0 eV of the hydrocarbon C_{1s} core level was used as a calibration for the absolute energy scale. Overlapping peaks were resolved into their individual components by using software supplied together with the XPS spectrometer. The detailed deconvolutions were based on a knowledge of binding energies and full widths at half maximum (FWHMs) from studies of corresponding homopolymers.

Contact Angle Measurement

The measurement of contact angle was performed at 20°C (contact time, 30 s) by the sessile drop method, employing a contact-angle measurement apparatus (Type JY-82, made by Chengde Instrument Factory, China). Drops of twice-distilled water (1.5–2.0 mm diameter) were dropped onto the surface of polymer film through a microsyringe. For each sample, a mean of six separate contact angle values was obtained and used to evaluate the hydrophilicity of PMMA-g-PEO graft copolymers.

Transmission Electron Microscopy (TEM)

TEM was performed on ultrathin films which were cast from 0.05% W/V polymer solutions in CHCl₃ on the surface of water. Grids were placed on the top of the film and the grids with films were lifted from the water surface using glass slides. Samples (grids with ultrathin films) were exposed to OsO₄ vapor and observed and micrographed with a transmission electron microscope (JEM 200CX, JEOL).

Differential Scanning Calorimetry (DSC)

DSC experiments were carried out using a Perkin-Elmer DSC-2C instrument. The heating rate was 10 K/min.

Thin polymer films with and without solvent treatment were used as samples. The weight of sample used was about 8 mg.

Scanning Electron Microscopy (SEM)

The surface morphology of thin polymer films with and without solvent treatment was recorded using JSM-T330A SEM. The samples' surfaces were coated with a thin layer of gold-palladium. This coating was carried out by placing the samples in a high-vacuum evaporator and sputtering with the gold metal held in a heated tungsten basket.

RESULTS AND DISCUSSION

Microphase Separation Structure

Ultrathin PMMA-g-PEO films were subjected to TEM. Osmium tetroxide was used for contrasting the phases. OsO₄ binds efficiently to PEO structures, while the film prepared from PMMA homopolymer shows a homogeneous structure in TEM with no apparent binding of OsO₄ (no photographs present).

The TEM photographs of PMMA-g-PEO are presented in Fig. 1 as dark areas due to the binding of OsO₄ to PEO segments. For the copolymers with shorter PEO side chains (M_n of PEO, 1650), it is difficult to observe microphase separated structure. Only when PEO component content is nearly equivalent to PMMA in the copolymer, a blurred structure could be observed (see Fig. 1a). This could be ascribed to the better phase compatibility of shorter PEO side chains with PMMA backbones. One PEO side chain has only one free end, while its other end binds to the PMMA backbone, which would promote mutual compatibility of these two components.

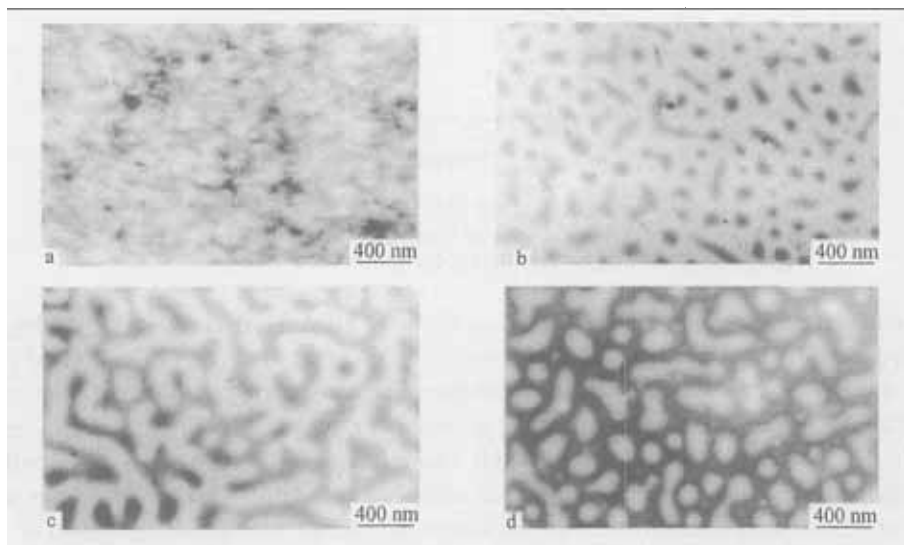


Fig. 1 TEM photographs of PMMA-g-PEO copolymers, contrasted with OsO₄. The dark areas are PEO-rich domains with bound OsO₄.
a) Sample B; b) Sample F; c) Sample H; d) Sample J

The graft copolymers having longer PEO side chains (M_n of PEO, 3200) can readily undergo microphase separation and the shape and the size of domains depend on the copolymer composition. Copolymer F (EO, 38.0 mol%) presents an “island-sea” structure (PEO phase is the “island” and PMMA is the “sea”) (Fig. 1b); Copolymer H (EO, 56.5%) shows an “network” (Fig. 1c) structure; and copolymer J (EO, 74.1 mol%) represents an “inverse island-sea” (PMMA phase is the “island” and PEO is the “sea”) structure (Fig. 1d).

In conclusion, the length of PEO side chain plays a significant role in the occurrence of microphase separation for PMMA-g-PEO. The graft copolymers having longer PEO side chains (M_n of PEO, 3200) readily exhibit a microphase separated structure.

Crystallinity

PEO homopolymers are semicrystalline and PMMA homopolymers are amorphous. We would like to know whether PEO side chains can also crystallize in PMMA-g-PEO. The crystallinity of the copolymers was investigated by DSC using thin polymer film samples with and without solvent treatment. Compared with parent semicrystalline neat PEO homopolymer with melting point of 55°C and PMMA homopolymer without melting point, the graft copolymers show modified thermal properties. Solvent treatment also has a great effect on thermal properties. The results are summarized in Table 2 and some typical DSC thermograms demonstrating the described features are shown in Fig. 2.

Table 2. The fusion heat ΔH (J/g) and melting temperature T (°C) of PMMA-PEO copolymer I with and without solvent treatment and PEO homopolymer

Sample	PMMA-g-PEO					PEO
	Without treatment	Ethyl alcohol	Water	Petroleum ether	Cyclohexane	
ΔH (J/g)	0.8	0	0	2.79	1.26	110.71
T (°C)	45.3; 48.0	–	–	45.4, 47.5	47.4, 54.4	55.0

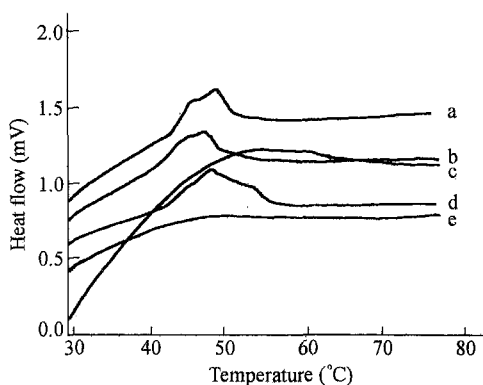


Fig. 2 DSC thermograms of the PMMA-g-PEO copolymer (Sample I) with solvent treatment (a) without treatment, (b) cyclohexane, (c) ethyl alcohol, (d) petroleum ether and (e) water

Graft polymer I exhibits melting endotherms at about 48°C. A great decrease in melting point and ΔH compared with parent PEO homopolymer is due to the incorporation of PEO side chains into the graft copolymer and indicates a major phase compatibility. The endotherm at 48°C corresponds to the melting of crystalline regions of PEO segments, thus it also indicates the presence of a separated PEO phase with a certain degree of crystallinity. In the copolymers with shorter PEO side chains (M_n of PEO, 1650) or at a low bulk PEO content, for graft copolymer A to G, no melting endotherm was observed. This might be due to an increased phase compatibility of PEO within dominant PMMA backbones and insufficient phase separation or because of the amorphous structure of PEO phase.

To study the effect of solvent treatment on crystallinity, graft copolymer I was chosen because of its longer PEO side chains and higher PEO content. The graft copolymer I film treated with water or ethyl alcohol does not exhibit melting endotherms again at about 48°C, indicating that there is no crystalline regions of PEO side chains. Because water and ethyl alcohol are good solvents for PEO, therefore, PEO side chains in the copolymers were dissolved and PEO crystals destroyed. On the other hand, for graft copolymer I film which has been treated with cyclohexane or petroleum ether, there still exist melting endotherms and even slight greater ΔH values compared with untreated sample, implying a slight increase of PEO crystals in cyclohexane and petroleum ether. The reason might be that cyclohexane and petroleum ether are poor solvents for PEO, and will be discussed later. Figure 2 shows that the melting peaks are all irregular. This might be due to incomplete crystallinity of PEO domains.

Surface Morphology

Scanning electron microscopy (SEM) was used to investigate the surface morphology of PMMA-g-PEO films with and without solvent treatment. Some white bulges on the film surface of graft copolymer I were observed (see Fig. 3a). These white bulges may correspond to the semicrystalline domains of PEO which were in accord with the finding of a melting endotherm of PEO crystalline phase by DSC in the graft copolymer I film. After surface treatment with ethyl alcohol, these white bulges disappeared, and the surface of the film became smoother (Fig. 3b). On the other hand, cyclohexane surface treatment led to slightly bigger white bulges, indicating the greater semicrystalline domains of PEO on the surface (Fig. 3c). The morphology results accord with the findings by DSC.

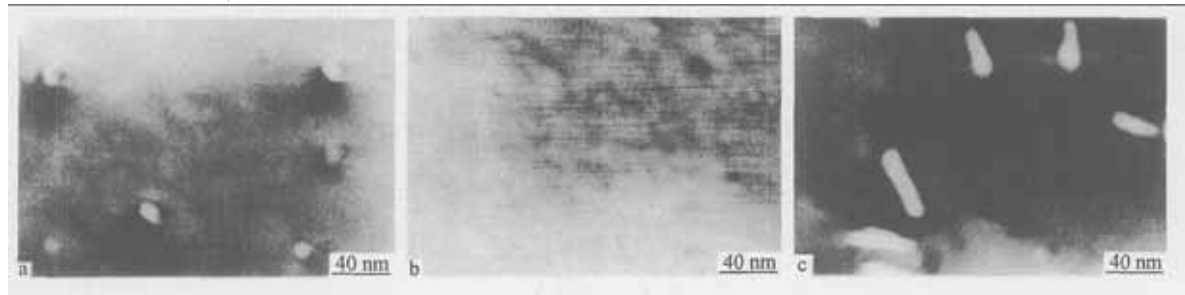


Fig. 3 SEM photographs of the PMMA-g-PEO copolymer (Sample I) with solvent treatment
a) Without treatment, b) Ethyl alcohol, c) Cyclohexane

Surface Composition

The effects of bulk structural parameters (the bulk composition and PEO side chain length) on the surface composition of PMMA-g-PEO were reported previously^[11]. In this study we are concerned with the changes in the surface chemistry of polymer film after surface treatment with solvent. Many multicomponent polymer systems have been reported to undergo surface rearrangements. The change of contacting medium always triggers surface restructuring in order to minimize interface free energy.

Water, ethyl alcohol, cyclohexane and petroleum ether were chosen as solvents for surface treatment. Water and ethyl alcohol are good solvents for PEO and extremely poor solvents for PMMA, while cyclohexane and petroleum ether are poor solvents for both PEO and PMMA. The results in Table 3 and Fig. 4 show that

Table 3. The effect of solvent treatment on the surface PEO content of PMMA-g-PEO copolymer I

Sample	Bulk EO (mol%)	Solvent	Surface EO (mol%)
F	38.0	Untreated	9.1
		Cyclohexane	20.8
		Petroleum ether	18.2
		Ethyl alcohol	16.7
		Water	10.0
G	49.2	Untreated	31.9
		Cyclohexane	48.0
		Petroleum ether	50.0
		Ethyl alcohol	28.9
		Water	28.9
H	56.5	Untreated	52.0
		Cyclohexane	59.4
		Petroleum ether	58.4
		Ethyl alcohol	41.7
		Water	50
I	65.2	Untreated	80
		Cyclohexane	100
		Petroleum ether	100
		Ethyl alcohol	73.3
		Water	73.3

solvent treatment causes the change of surface composition or surface rearrangements, and the surface structural change varies with solvents treated.

Figure 4 gives the C_{1s} XPS core level spectra of the graft copolymer I films with and without solvent treatment. The peak at about 286.5 eV for the C_{1s} levels is attributable to the carbons singly bonded to oxygen of both PMMA and PEO segments, in reference to hydrocarbon, which is at 285 eV. The peak corresponding to the carbonyl carbons of PMMA segments is at about 288.8 eV. The PEO component content can be calculated through the deconvolution of the C_{1s} spectra and from the signal intensities for each of the components, mainly reflected by the relative intensity of the peak at 286.5 eV. The spectrum for the graft copolymer I film treated with cyclohexane or petroleum ether shows a single peak at 286.5 eV, corresponding to the carbons singly bonded to oxygen and without the appearance of peaks at 285 and 288.6 eV which are assigned to the carbonyl- and hydrocarbon-type carbons, indicating the presence of only PEO components on the surface.

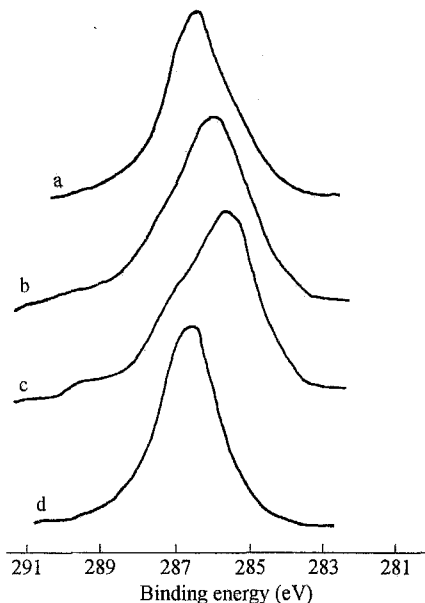


Fig. 4 C_{1s} core level XPS spectra for the PMMA-g-PEO copolymer (Sample I) with solvent treatment
a) Without treatment, b) Water, c) Ethyl alcohol; d) Cyclohexane or petroleum ether

In most cases, for the same graft copolymer, the surface contents of PEO are as follows:

Surface treated with petroleum ether or cyclohexane > Surface untreated > Surface with water or ethyl alcohol

When treated with water or ethyl alcohol, the PEO segments might swell, disentangle and dissolve in the surface phase, and swell in the bulk phase. However, the movement of PMMA segments does not occur, because PMMA is insoluble in water or ethyl alcohol and is in the glass state. During the drying process of copolymer films in vacuum after water or ethyl alcohol treatment, PEO component will rearrange in the surface phase. PEO segments tend to move into the bulk in order to lower the surface free energy, resulting in a lower PEO content in the surface, compared with untreated surface, because PEO has a higher surface free energy than PMMA (the surface energies of PMMA and PEO are 4.02 N/m and 44 N/m, respectively). Thus, treatment with water or ethyl alcohol can indeed be regarded as instigating a process in which PEO segments rearrange in the surface phase to minimize surface free energy. The change of surface and bulk structure for the graft copolymer was verified by the findings of DSC and SEM.

Cyclohexane or petroleum ether treatment increases the PEO component content on the surface. As cyclohexane or petroleum ether is a poor solvent for both PMMA and PEO, and PEO segments are in a highly elastic state and have excellent flexibility and mobility, it is speculated that PEO domains with a certain degree of crystallinity in the surface phase might develop in the poor solvent. Although the surface with increased PEO component may have a higher surface free energy, the PEO crystals of PEO domains located in the surface phase might compel it to keep stable by acting as physical crosslinkers.

Surface Hydrophilicity

Contact angle measurement was used to characterize the surface hydrophilicity of PMMA-g-PEO. In general, for the same graft copolymer, θ s decreases as the film surface is treated with petroleum ether or cyclohexane, *i.e.* surface hydrophilicity is increased. However, surface treatment with water or ethyl alcohol will increase the θ s, *i.e.* surface hydrophilicity is decreased (see Table 4). This is due to the change of surface hydrophilic PEO content caused by surface solvent treatment, which has been discussed previously. The hydrophilicity results also show that solvent treatment affects the surface properties of PMMA-g-PEO.

Table 4. The effect of solvent treatment on surface hydrophilicity of PMMA-g-PEO (data are expressed as the mean average of six determination for each sample, SE is 1 or 2)

Sample	A	B	C	D	E	F	G	H	I	J
θ_s (°)	66	64	56	52	26	67	63	49	14	14
θ_1 (°)	54	46	41	45	24	64	55	44	—	—
θ_2 (°)	47	45	43	43	17	54	50	41	14	—
θ_3 (°)	67	65	60	61	52	67	64	54	—	—
θ_4 (°)	67	66	53	—	—	65	60	52	30	—

θ_1 , θ_2 , θ_3 , or θ_4 represents the contact angle of water of a PMMA-g-PEO film treated with petroleum ether, cyclohexane, ethyl alcohol or water respectively and θ_s is the contact angle of water on a PMMA-g-PEO film without solvent treatment.

CONCLUSION

The surface and bulk structural morphology of PMMA-g-PEO was characterized by DSC, TEM, SEM and contact angle measurement. It is evident that solvent treatment has great influence on the surface morphology and properties of copolymer films. For the same graft copolymer, petroleum ether or cyclohexane treatment results in increased surface PEO content or better hydrophilicity, whereas water or ethyl alcohol treatment causes a reverse effect. Graft copolymer I, having longer PEO side chains and higher PEO content, presents a separated PEO phase with even a certain degree of crystallinity on the surface. Semicrystalline PEO domains on the surface were destroyed by water or ethyl alcohol treatment. However, surface treatment with petroleum ether or cyclohexane favors their growth. The excellent flexibility, mobility and crystallinity as well as solubility of PEO side chains in different solvents play a significant role in the formation of structured surface during and after solvent treatment. Graft copolymer with longer PEO side chains (M_n of PEO, 3200) may readily undergo microphase separation and the shape and size of domains depend on the copolymer's composition. Shorter PEO side chains favor phase compatibility of PEO and PMMA segments in the graft copolymer.

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