Preparation and properties of MPEG-grafted EAA membranes via thermally induced phase separation

Jing Zhou a,b, Jie Yin a,b, Rui Lv a,b, Qiangguo Du a,b,*, Wei Zhong a,b

a Department of Macromolecular Science, The Key Laboratory of Molecular Engineering of Polymer, Ministry of Education, Shanghai 200433, PR China
b Fudan University, Shanghai 200433, PR China

Received 1 February 2005; received in revised form 17 May 2005; accepted 7 June 2005
Available online 19 July 2005

Abstract

Graft reaction of poly(ethylene glycol monomethyl ether) (MPEG) onto poly(ethylene-co-acrylic acid) (EAA) through the esterification reaction of carboxyl groups on EAA chain with hydroxyl end groups in MPEG was performed. The results showed that the grafting degree increased with reaction time. Water contact angle measurements and protein adsorption experiments indicated that the hydrophilicity and antifouling properties of films were improved after EAA was grafted with MPEG. The microporous membranes of EAA grafted with MPEG (EAA-g-MPEG) and EAA were prepared via thermally induced phase separation (TIPS) process with di-n-octyl phthalate (DOP) as solvent. Phase diagrams for those systems were determined by time-resolved light scattering (TRLS) and differential scanning calorimetry (DSC). It was found that the binodal curve shifted to the lower temperature after EAA was grafted with MPEG, while changes of the dynamic crystallization temperatures were rather small. The membrane morphologies were investigated, which revealed that the pore sizes of EAA-g-MPEG membranes were smaller than those of EAA membranes.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Poly(ethylene-co-acrylic acid); Poly(ethylene glycol monomethyl ether); Graft; TIPS; Hydrophilicity

1. Introduction

Thermally induced phase separation (TIPS) is one of the most popular methods to make macroporous membranes [1,2]. In general, a homogeneous solution is prepared at an elevated temperature by blending the polymer with a diluent of high-boiling point, then the solution is cooled to induce solid–liquid (S–L) or liquid–liquid (L–L) phase separation, and finally a microporous structure is formed after the diluent is extracted by a volatile solvent [3]. This method is also applicable to crystalline polymers that cannot be used in the traditional solution membrane formation due to solubility problems. TIPS membrane formation has attracted plenty of research interests since 1980s, and microporous membranes of various polymers such as polypropylene, polyethylene, polysulfone and poly(methyl methacrylate) have been prepared using this method [4–7]. Membranes made of such polymers have good thermal stability and chemical resistance. However, the relatively poor hydrophilicity of these membranes limits their applications in water treatment, for the loss of permeation flux caused by adsorptive fouling of biological molecules, such as proteins on the surface and even inside the pores. Fouling reduces productivity due to longer filtration times and shortens membrane life due to the harsh chemicals used for cleaning [8]. Thus, hydrophilic microporous membranes are desirable. But the conventional hydrophilic polymers such as poly(vinyl alcohol) and cellulose acetate are usually poor in thermal stability and chemical resistance [9]. An alternative way is to make the surfaces of hydrophobic membranes hydrophilic by physical and chemical modifications, such as adsorption of surfactant on membrane surface, plasma treatment, and surface grafting with hydrophilic species [10,11]. However, thermal instability and
technical complexity of these membranes made them undesirable in practical application. Therefore, an ideal way is to make stable macroporous membranes from copolymers consisting of both hydrophobic and hydrophilic components. Copolymerizing ethylene with hydrophilic monomers such as vinyl alcohol or acrylic acid can be used to improve hydrophilic properties of ethylene-based polymeric membranes. Most of these polymers are crystalline or semi-crystalline polymers and can be made into membranes with high strength and stability through TIPS process. Many studies have been reported on poly(ethylene-co-vinyl alcohol) (EVOH), which is a semi-crystalline random copolymer with good wet strength with hydrophilicity [12,13]. There are also reports on porous EVOH membranes prepared via TIPS process using PEG, DMSO or glycerol as diluents [14–16]. Poly(ethylene-co-acrylic acid) (EAA) is another ethylene-based crystalline copolymer with hydrophilic groups. Its hydrophilicity is better than polyethylene due to the introduction of small amount of acrylic acid groups on the ethylene backbone. Though the aryllic acid groups have certain effect on the regularities of molecular chain arrangement, EAA is a semi-crystalline polymer with good film performance, mechanical strength and chemical resistance. Effects of initial polymer concentrations and cooling rates on the membrane morphologies of EAA and EAA-g-MPEG were discussed.

2. Experiment

2.1. Materials

Ethylene-acrylic acid copolymer (Primacor1410) was purchased from Dow chemical and high density polyethylene (HDPE) DMD7006 was purchased from QiLu Petrochemical Co. Ltd., China. The properties of these polymers are summarized in Table 1. MPEG (average $M_w = 350$) was purchased from Acros Organics. DOP and methanol (analytical purity) were purchased from Shanghai Chemical Reagents Co. All chemicals were used without further purification.

2.2. Grafting reaction

EAA and DOP (1:20, w/w) were added to a flask fitted with a condenser, a stirrer, and an inlet for nitrogen. MPEG was quickly added when the mixture was heated to 180°C. The mixture was completely homogeneous and was kept at 180°C to react for a predetermined time ranged from 2 to 8 h. After this, the mixture was precipitated in methanol, filtered and washed with excess methanol repeatedly. Finally the product was dried in vacuum at 50°C to constant weight. The grafting degree (DG) and the extent of grafting reaction $P$ were calculated by the following equations:

$$DG(\%) = \left(\frac{w_B - w_0}{w_0}\right) \times 100 \quad (1)$$

$$P(\%) = \left(\frac{w_G - w_0}{w_0}\right) \times 100 \quad (2)$$

where $w_0$ and $w_G$ are the weight of EAA before and after grafting reaction (EAA-g-MPEG) and $w_G$ is the calculated weight increment of EAA supposing all carboxyl groups are esterified.

2.3. Characterization of EAA and EAA-g-MPEG

The samples were hot pressed at 200°C between two iron plates coated with polytetrafluoroethylene and cooled in the air. The obtained films were washed with acetone and dried.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Acrylic acid content (wt.%)</th>
<th>Melt index (g/10 min)</th>
<th>Density (g/cm³)</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EAA1410</td>
<td>9.7</td>
<td>1.5</td>
<td>0.938</td>
<td>99°</td>
</tr>
<tr>
<td>HDPE</td>
<td>–</td>
<td>5.0</td>
<td>0.959</td>
<td>130</td>
</tr>
</tbody>
</table>

* Determined by DSC.
at vacuum before measurement. To investigate the changes in chemical structure after grafting, attenuated total reflectance infrared spectra (ATR-FT-IR) of the polymer films and IR spectrum of MPEG were obtained using a FT-IR spectrometer (NEXUS470).

The static contact angle of EAA, EAA-g-MPEG and HDPE films were measured using a contact angle goniometer (Dataphysics OCA15). Droplets of distilled water (2 μl) were dropped at different places of the films and at least 10 readings were taken to determine average values.

Bovine serum albumin (BSA) was used as a model protein to evaluate the protein fouling characteristics of films [19]. The static BSA adsorption experiments were performed as follows: 0.1 M Tris–HCl buffer solution (pH 8.0) was first prepared [20], then carefully weighed BSA was added to prepare solutions of BSA concentrations from 0.1 to 5 mg/ml. The standard curve of BSA solutions was determined at 280 nm using a spectrophotometer (Perkin Elmer, Lambda 35). The films with the same external surface area (28 cm²) were added into BSA solutions with different concentrations. The mixture was incubated at 30 °C for 36 h to reach adsorption–elution equilibrium. The amounts of protein adsorbed on the membrane surface were calculated from the change of BSA concentrations, which were determined on the basis of the absorbance at 280 nm and the standard curve of BSA solutions. Measurements of triplicate samples were performed and averaged.

The viscosities of EAA and EAA-g-MPEG were determined by ARES (Rheometric Scientific), with the dynamic frequency scanning from 0.1 to 10 rad/s at 1% strain at 160 °C. The diameter of the parallel plates was 25 mm and the distance between the two plates was 1.7 mm.

2.4. Determination of phase diagrams

EAA or EAA-g-MPEG was blended with DOP in a flask equipped with a nitrogen inlet, a condenser and a stirrer. The mixture was maintained at 180 °C until homogeneous, and then quenched in liquid nitrogen. The quenched samples were used for the determination of phase diagrams and scanning electron microscopy (SEM) observation.

Time-resolved light scattering (TRLS) was used to determine the binodal lines for the two polymer–diluent systems [21–23]. Fig. 1 shows a schematic diagram of the equipment. A He–Ne laser (15 mW) was used as the light source (λ = 632.8 nm). Between the light source and the sample a polarizer and an attenuator were set. The light scattered from the sample was recorded by a CCD camera. During the measurement, a small piece of sample was placed between a pair of microscope cover slips. To prevent diluent from evaporating, a Teflon film of 130 μm thickness with a square opening in the center was inserted between the cover slips. Each sample was heated on a hot stage at 180 °C for 5 min, then was cooled at a rate of 1 °C/min. Every 5 s the image and the temperature of the sample were recorded simultaneously. From the pictures, a plot of the scattered light intensity, I, against the wavenumber q was obtained. The wavenumber q is given by Eq. (3):

\[ q = \frac{4\pi n}{\lambda} \sin(\theta/2) \]  

where n is the refractive index of the solution, λ the wavelength of the light in vacuum, and θ is the scattered angle [23]. The temperature at which the scattered light intensity at a certain scattered angle just started to rise was taken as the phase separation temperature. For the sake of reliability, three measurements for each sample were performed and averaged.

DSC (Perkin Elmer DSC-7) was used to determine the crystallization temperature (Tc). About 3-5 mg sample was sealed in an aluminum DSC pan, melted at 160 °C for 5 min and then cooled at a rate of 2 °C/min to 50 °C. The onset of the exothermic peak during cooling was taken as the crystallization temperature.

---

Fig. 1. Schematic diagram showing time-resolved light scattering apparatus.
2.5. SEM observation

Homogeneous polymer–diluent mixtures were prepared as above. The quenched sample was chopped into small pieces, sealed with two cover slips and heated on the hot stage at 180 °C for 5 min as described above. The sample was then either cooled in air of 30 °C and in water of 60 °C. The cooling rate of sample was measured using a thermocouple buried in the sample. The cooling rate in air of 30 °C and in water of 60 °C was 13 and 1.5 °C/min, respectively. The difference of cooling rate is attributed to the difference in heat transfer coefficient. Then the samples were fractured in liquid nitrogen. After being extracted by methanol for 24 h, the sample was dried in the air overnight at room temperature. The cross-section of the sample was coated with gold-palladium and observed by a scanning electron microscope (JSM-5610LV).

3. Results and discussion

3.1. Grafting reaction of MPEG

Fig. 2 shows the effect of the reaction time on the grafting degree (DG) and the extent of grafting reaction P. After 8 h reaction the grafting degree reached 27.2% and about half of the carboxyl groups were grafted with MPEG chain. It can be seen that DG and P increased with reacting time, which means that the extent of grafting reaction can be easily controlled through reacting time. Fig. 3 shows IR spectra of EAA, EAA-g-MPEG (DG = 18.1 wt.%) and MPEG. EAA film showed the characteristic absorbance band for carboxyl at 1703 cm⁻¹ (Fig. 3b). Converting carboxyl into ester group could be confirmed by the appearance of absorbance band at 1737 cm⁻¹ (Fig. 3a). Moreover, the characteristic C=O band of MPEG at about 1110 cm⁻¹ (Fig. 3c) could be easily found in Fig. 3a, clearly indicating that MPEG had been grafted onto EAA chain. Since ATR-FT-IR spectroscopy is commonly used to characterize the chemical changes on the surface layer, results also indicated the existence of hydrophilic MPEG chain on the film surface.

3.2. Hydrophilicity and protein adsorption properties

Contact angle measurements have been commonly used to characterize the relative hydrophilicity or hydrophobicity of polymer surface [24,25]. However, such measurements are difficult to interpret for synthetic porous membranes, for their surface properties are also affected by many other factors such as capillary forces within pores, contraction in the dry state, heterogeneity, roughness and restructuring of the surfaces [20]. Nevertheless, the relative hydrophilicity or hydrophobicity of each sample can be easily obtained by this method. In this study, compact films with flat surface were prepared and measured. The static water contact angles of HDPE, EAA, EAA-g-MPEG membranes are listed in Table 2. For HDPE film the contact angle was 104.8°, indicating that it was hydrophobic. The contact angle of EAA film was lower than HDPE film’s because of the existence of carboxyl groups. Nevertheless, the data remained relatively high, since EAA contained acrylic acid of only 9.7 wt.%. The contact angle of EAA-g-MPEG film (DG = 18.1 wt.%) was 81.6° and lower than EAA film, owing to the introduction of MPEG’s hydrophilic chains. Comparing EAA-g-MPEG(a) and EAA-g-MPEG(b) in Table 2.

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Maximum</th>
<th>Minimum</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>105.0</td>
<td>102.5</td>
<td>104.8</td>
</tr>
<tr>
<td>EAA</td>
<td>90.6</td>
<td>85.8</td>
<td>88.8</td>
</tr>
<tr>
<td>EAA-g-MPEG</td>
<td>83</td>
<td>78.5</td>
<td>81.6</td>
</tr>
<tr>
<td>EAA-g-MPEG</td>
<td>81</td>
<td>70.9</td>
<td>74.8</td>
</tr>
</tbody>
</table>

DG = 18.1 wt.%;
DG = 27.2 wt%.

![Fig. 2](image-url) | **Fig. 2.** The grafting degree and extent of grafting reaction for EAA-g-MPEG.

![Fig. 3](image-url) | **Fig. 3.** The IR spectroscopy of (a) EAA-g-MPEG (DG= 18.1 wt.%); (b) EAA and (c) MPEG.
with EAA-g-MPEG(b), it can be seen that the hydrophilicity increased with grafting degree. This was because more MPEG chains distributed on the film surface when the grafting degree increased. From above it is clear that by grafting MPEG to EAA the hydrophilicity of EAA film was effectively improved. Moreover, the hydrophilic groups existed on the film surface, which was consistent with the result from ATR spectra.

In terms of applications, membrane fouling should be reduced as much as possible, especially for water treatment. Usually, a hydrophilic surface will suppress the adsorption of biomolecules or cells on the membrane and reduce fouling. In the present study, BSA was selected as a model protein to evaluate the protein fouling properties of membranes. The BSA adsorption experiment was performed with two BSA concentrations. Table 3 shows the results of BSA adsorption experiment. It can be seen that for BSA solution of 0.65 mg/ml, the adsorption on EAA film was 92 ± 6 μg/cm², compared with 141 ± 10 μg/cm² on HDPE film. This can be ascribed to the higher hydrophilicity of EAA film than that of HDPE film. For BSA solution of concentration 1.13 mg/ml, the consistent result was obtained. The films of EAA-g-MPEG showed lower BSA adsorptions than EAA film, indicating that antifouling properties had been improved effectively. Meanwhile, the amount of BSA adsorbed on the film surface decreased obviously with the increase of the grafting degree. It was also found that a higher BSA concentration could lead to an increase of BSA adsorbed on the film. However, it was noticed that the difference of the adsorption amount between EAA and EAA-g-MPEG was more remarkable than that of the contact angle data, which is shown in Table 2. It seems that hydrophilicity was not the only factor that impacted the antifouling properties. From the literature, PEG as a surface modifying agent is the most effective macromolecules for reducing bioadhesion [17]. The majority of the models of grafted PEG attribute their protein resistance to two main factors, (i) the steric or osmotic repulsion between proteins and the chains and (ii) the assumption that the CH₂CH₂O segments completely repel protein [26].

### Phase diagrams

During the process of phase separation, the heterogeneous system caused by phase separation will lead to light scattering due to the difference in refractive index of the phases. Therefore, the phase separation temperature can be determined from the appearance of scattering light during cooling.

In this study, the phase separation temperature was defined as the temperature at which the light intensity at a given wavenumber \( q \) started to rise, as shown in Fig. 4. It can be seen that the light intensity was constant at first, and started to rise at a time when scattering light appeared. This time was the incipient time of phase separation, and the corresponding temperature recorded by the computer was taken as the phase separation temperature. As the temperature continued to drop the scattering light intensity increased with elapsed time, implying that the size of the phase-separated structure increased, as shown in Fig. 5. It is known that the phase separation temperature is influenced by the cooling rate. Only when the cooling rate approaches to zero can the phase separation temperature be assumed to be the binodal temperature in L-L phase separation region. In this study, samples were cooled at 1 °C/min, which was a relatively slow cooling rate. Therefore, the phase separation temperatures were assumed to be binodal temperatures in L-L phase separation region.

It was noticed that when the phase separation occurred at the temperature above the crystallization temperature, \( I_q \) monotonically decreases with increasing \( q \) as shown in Fig. 5. This suggested that at this period the phase separation occurred via the nucleation and growth (NG) mechanism instead of the spinodal decomposition (SD) mechanism [27]. This is reasonable because NG is the expected mechanism when a system leaves the thermodynamically stable condition.
tion and slowly enters the metastable region of the phase diagram, while spinodal decomposition takes place in a fast quench into the two phase region limited by the spinodal curve.

Fig. 6 shows the phase diagrams of polymer-diluent systems, EAA with DOP and EAA-g-MPEG with DOP, respectively. The grafting degree of EAA-g-MPEG sample used was 8.7 wt.%. The phase separation temperatures in liquid–liquid (L–L) phase region represent the binodal curves as an approximation, and those in solid–liquid (S–L) phase region, which were measured by DSC, represent the crystallization temperatures. As shown in Fig. 6, these are typical phase diagrams for semi-crystalline polymers which display monotectic points at approximately 55–60 wt.% for the two systems. Upon cooling, for homogeneous melt with a polymer concentration less than monotectic point, liquid–liquid phase separation took place first and followed by crystallization in the polymer-rich phase. For homogeneous mixture with a polymer concentration greater than monotectic point, solid–liquid phase separation occurred prior to liquid–liquid phase separation.

As shown in Fig. 6, the binodal curve shifted to the lower temperature region after EAA was grafted with MPEG chain, while changes of the dynamic crystallization temperatures were rather small. This can be explained in terms of the Flory-Huggins theory [28,29]. It is well known that the binodal line shifts to higher temperature when polymer–diluent interaction parameter $\chi$ becomes more positive (that is, the system becomes less compatible) [3]. In reverse, when the polymer–diluent system becomes more compatible, the binodal line shifts to lower temperature. DOP can dissolve EAA above 160 °C and can dissolve MPEG at room temperature, which indicates that the MPEG-DOP system is more compatible than EAA–DOP system. After EAA backbone was grafted with MPEG chain, a more compatible component was introduced. Therefore, the grafted EAA–DOP system became more compatible than EAA–DOP system, and the binodal line shifted to lower temperature. The small changes of the dynamic crystallization temperatures can be explained as follows. EAA is a random copolymer whose tendency to crystallize is closely related to the number and length of the crystallizable ethylene segments [30]. During graft reaction, the hydroxyl end groups of MPEG reacted with carboxylic acid groups of EAA chain and formed branches of esterified MPEG. Thus the amount and length of ethylene segments in EAA backbone did not change. Moreover, the MPEG chain ($M_w = 350$) was much shorter than the backbone and the grafting degree was relatively small (DG = 8.7 wt.%). Therefore, the crystalline property of EAA was not much influenced by the grafting reaction and the crystallization temperatures changed little.

### 3.4. Membrane morphology

Fig. 7 shows the membrane morphologies formed by cooling in air of 30 °C and with polymer concentrations of 30 wt.% (Fig. 7a and b) and 60 wt.% (Fig. 7c and d). As shown in Fig. 6, liquid–liquid TIPS occurred prior to crystallization in the case of 30 wt.%, while the crystallization occurred first in the case of 60 wt.%. Fig. 7a and b are the images of cellular pores which are the typical structures resulted from L–L phase separation [3]. When the homogeneous polymer–diluent solution was cooled from one-phase region to a temperature corresponding to a two-phase region, the solution separated into a polymer-rich continuous phase and a polymer-lean droplet phase. The droplets continued to coarsen until their growth was arrested by solidification of the polymer-rich phase via crystallization. Since the final temperature (30 °C) was below the crystallization temperature of EAA or EAA-g-MPEG, as shown in Fig. 6, the L–L TIPS was followed by crystallization. In Fig. 7c and d, blocks of spherulites were observed, with many cellular pores on the interface of spherulites. This meant that morphologies resulting from S–L and L–L phase separation coexisted. It is possible to speculate on the mem-
brane formation mechanism as follows. Upon the cooling of the homogeneous polymer–diluent solution, it underwent S–L phase separation and formed polymer spherulites surrounded by a liquid phase. As the temperature decreased, the liquid phase followed the melting point depression curve until the monotectic point was reached. Below the monotectic temperature, the remaining solution phase underwent L–L phase separation as described above. Therefore, the blocks of spherulites were the results from EAA or EAA-g-MPEG crystallization, and the cellular pores on the interface of spherulites were likely to be the results from collisions of growing polymer-lean droplets. Comparing Fig. 7a and b with c and d, it was concluded that the pore sizes in 30 wt.% samples were larger than those in 60 wt.% samples. The reason has been discussed in literature [9].

Fig. 8 shows the membrane morphologies formed by quenching in water of 60 °C. Comparing Fig. 7a and b with Fig. 8a and b, it can be seen that the pore sizes of samples formed at slow cooling rate were larger, which indicated that smaller pore sizes could be fabricated by increasing cooling rate. As the cooling rate increased, there was less time for droplets to coarsen and the pore sizes decreased.

However, for polymer solutions of 60 wt.%, there were significant differences between samples prepared at different cooling rates, as shown in Figs. 7c and d and 8c and d. In Fig. 8c and d, the pores were not only on the interfaces of spherulites but also inside the spherulites. This can be explained as follows. The phase diagrams in Fig. 6 were obtained at a slow cooling rate, while the samples in Fig. 8c and d were quenched at a high cooling rate. When the temperature dropped below the crystallization curve, the system quickly went through the crystallization curve and entered into the L-L phase region which could be extrapolated from binodal line, as shown in Fig. 9 [31]. The solution separated into a polymer-rich continuous phase and a polymer-lean droplet phase, meanwhile EAA or EAA-g-MPEG crystallized out of the polymer-rich phase to form spherulites. Thus the grown polymer-lean droplets were entrapped within the spherulites and resulted in pores inside the spherulites [3].

As shown in Fig. 8, the pore sizes of EAA-g-MPEG membranes were smaller than those of EAA membranes. Two factors might affect the pore size. Firstly, it was probably attributable to the shorter time for coarsening of the droplets, due to the smaller area between the binodal curve and $T_c$ curve shown in Fig. 6. Secondly, the long grafted MPEG chain might lead to higher viscosity in the polymer-rich phase, resulting slower coarsening of the droplets and smaller pore sizes. This can be supported by the viscosity data for MPEG-grafted EAA and EAA shown in Fig. 10.
Fig. 8. Micrographs of the cross-sections of EAA and EAA-g-MPEG membranes (cooled in 60 °C water). (a) 30 wt.% EAA; (b) 30 wt.% EAA-g-MPEG; (c) 60 wt.% EAA; and (d) 60 wt.% EAA-g-MPEG.

The samples in Fig. 7a and b were prepared at slow cooling rates. Effects of the two factors were relatively small in this case. Thus the difference of pore sizes between them was not obvious. Moreover, droplet growth rate might also depend on the polymer-diluent interfacial tension, which could also be changing in these polymers.

Fig. 9. Schematic phase diagram with extrapolated binodal line.

Fig. 10. Rheology properties for EAA and EAA-g-MPEG (DG = 8.7 wt.%).

4. Conclusion

The MPEG-grafted EAA can be obtained by the esterification reaction of carboxyl groups on EAA chain with hydroxyl end groups in MPEG. The effect of the reaction time on the grafting degree revealed that grafting degree increased with the increase of reaction time. Water contact angle and BSA
adsorption measurements demonstrated that the hydrophilicity and protein adsorption properties of EAA films were improved after being grafted with MPEG. The anti fouling property of MPEG-grafted EAA membrane has its potential in water treatment applications. Phase diagrams for the two systems were determined. The binodal curve shifted to lower temperature after EAA was grafted with MPEG, while changes of the dynamic crystallization temperatures were rather small. This indicated that the grafted EAA–DOP system was more compatible than EAA–DOP system. The pore sizes of EAA-g-MPEG membranes were smaller than those of EAA membranes, which could probably be ascribed to the shorter time for coarsening of the droplets and to the higher viscosity of the polymer-rich phase.

Acknowledgement

This project was subsidized by the Special Funds for Major State Basic Research Project (2003CB615705).

References