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Confined crystallization behavior of PEO in organic networks

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Abstract

Poly (ethylene oxide) (PEO) and poly (trimethopropane trimethacrylate) (PTMPTMA) interpenetrate networks have been synthesized. The confined crystallization behavior of PEO in the PTMPTMA networks has been investigated by a differential scanning calorimeter and scanning electron microscope. The degree of PEO crystallinity in PEO/PTMPTMA interpenetrate networks reduces with the increase of PTMPTMA. PEO is in an amorphous state when the concentration of PEO is lower than 50% in the interpenetrate networks system. The melting points of crystalline PEO in the networks are lower than that of pure PEO, and the melting point of PEO in the networks is higher and increases with the increase of PEO in the interpenetrate networks. Wide-angle X-ray diffraction results show that the PEO crystallite size perpendicular to the (120) plane is not affected as much as PEO in silica networks.

Keywords: PEO confined crystallization behavior; PTMPTMA networks

1. Introduction

The field of confined liquids, and in particular, that of confined polymers has developed rapidly in the last ten years. Confinement complicates the physics of such films and may alter their properties drastically [1–3]. Whereas bulk liquids have been investigated rather extensively [4–8], there are only a handful of quantitative investigations on fluid thin films [9–15], mainly due to difficulties in preparing samples with well-controlled thickness and interfacial environments. Much attention has been focused on the confined behavior of polymer films, and many interesting results have been reported [16–24], such as, the viscoelastic dynamics of confined polymer melts, the confinement-induced miscibility in polymer blends, the chain conformation in ultrathin polymer films, and the kinetics of chain organization in ultrathin polymer films, and so on. Computer simulations of polymer melts between impenetrable walls show that chain dimensions parallel to the surfaces are only slightly larger than in the bulk, and that the chain conformation in this direction remains gaussian. In contrast to these ideas, recent self-diffusion measurements for confined polymeric system are consistent with the notion that chain conformation is strongly modified. Similarly, Frank et al. have suggested that chain structure can be significantly affected in ultrathin films (that is thickness $D \leq 100$ nm). Preliminary scattering studies by Russell tentatively indicated that chain conformation is modified in the thin film geometry. Similarly, Reich and Cohen found that polymers of high molecular mass exhibited long-range order (up to 10 μm) from the substrate. Based on this, it is clear that even the most fundamental questions regarding the behavior of polymer chains near surfaces and interfaces are poorly understood. In this paper, we present a method to study the behavior of polymers in a confined environment, which differ from the behavior of polymer films less than a micrometer thick.

At present, most of the works on confined polymers are focused on polymer films and ultrathin polymer films. The design of new materials with enhanced properties continues to be a driving force for the investigation of new materials.

Poly (ethylene oxide) (PEO) is a simple and representative linear polymer with interesting behavior both in the blending with other polymers and in the pure state. Because of the fundamental importance and wide applications, many authors have studied the phase structure, morphology and crystallization in the solid state and in solution [25–38]. These studies have been carried out both in the pure polymer and in its blends, but the behavior of PEO in a confined environment has been less quantitatively understood, when compared with that of PEO in a free environment. The designed networks and the synthesis of the composite

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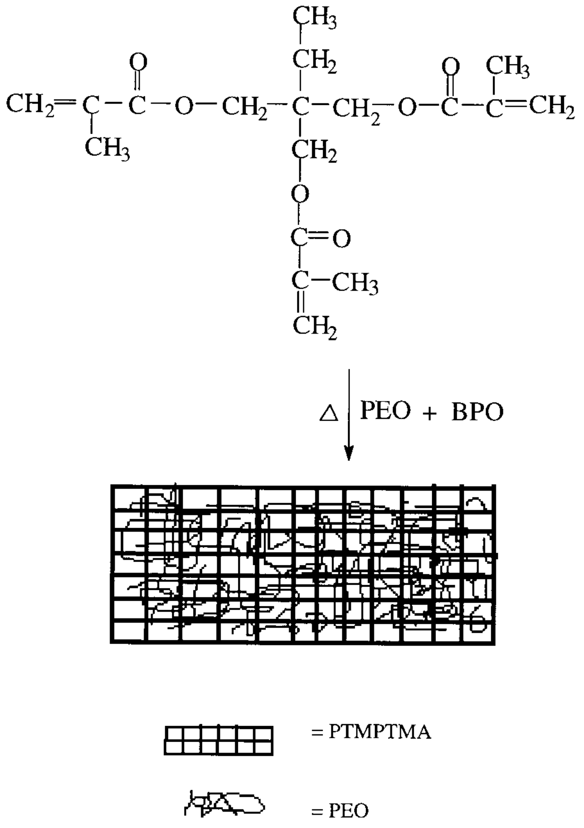

Scheme 1. The overall process of synthesis of PEO/PTMPTMA interpenetrate networks.

samples containing PEO and poly (trimethopropane trimethacrylate) (PTMPTMA) are shown in Scheme 1. During this process PTMPTMA becomes system of networks, and PEO will be embedded in the networks. This approach allows us to study the confined behavior of PEO in a well defined organic network intimately connected to various concentrations of polymer and to investigate the morphology and crystallization of PEO in the confined environment.

2. Experiment

The PEO here is a commercial product of Polysciences Inc. The M_w and M_n determined by gel permeation chromatography (GPC) are 19 000 and 10 200, respectively, and their ratio is 1.86. The trimethopropane trimethacrylate (TMPTMA) is synthesized in our laboratory. The general procedure for preparing the sample was to dissolve PEO in chloroform at a concentration of about 20 wt%. A measured amount of TMPTMA is mixed with a chloroform solution of PEO and a catalytic amount of benzoperoxide was added to the solution. A homogeneous solution was attained after stirring, the solution was heated to 80°C for 24 h until the TMPTMA polymerized completely. The samples were then placed in an oven at 80°C for one week until the solvent completely evaporated. The PEO remained in the molten state. The specimens thus prepared were further dried in a vacuum oven at 80°C until a constant weight was attained. A DSC experiment was performed with a Perkin–Elmer DSC-7 differential scanning calorimeter for the observation of melting and crystallization of PEO, a Philips PW 1700 automatic powder diffractometer with Ni-filtered CuKα radiation was used for the wide-angle X-ray diffraction (WAXD) measurements (the scans were obtained by using a 0.05° step programmed with a collection time of 10 s per step) and a scanning electron microscope (SEM) (Jeol JXA-840) was used to investigate the morphology of PEO and PTMPTMA interpenetrated networks fracture surface which were sputter-coated with gold.

3. Results and discussion

Fig. 1 shows the DSC curves of PEO/PTMPTMA interpenetrated networks with different ratios on heating. The samples were heated from 0 to 100°C with a heating rate of 10°C/min. In Fig. 1 the samples exhibit no peak when the PEO weight percentage is under 50%. This result indicates that the crystallization of PEO in the networks is strictly confined.

Fig. 2 shows the DSC results of the interpenetrate networks. The weight percentage of crystalline PEO evolved was recorded vs. the concentration of PEO in the composite samples. The heat of fusion obtained is directly proportional to the weight percentage of crystalline PEO. The weight percentage of crystalline PEO (C_r, wt%) was

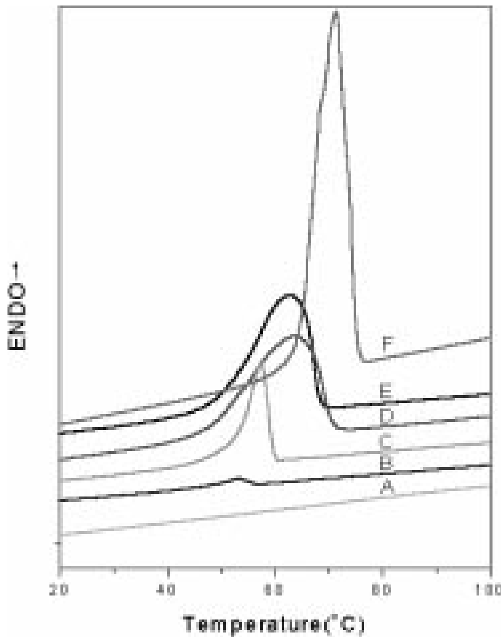

Fig. 1. DSC curves of PEO/PTMPTMA interpenetrate networks. (A: 50 wt% PEO, B: 60 wt% PEO, C: 70 wt% PEO, D: 80 wt% EPO, E: 90 wt% PEO, and F: pure PEO).

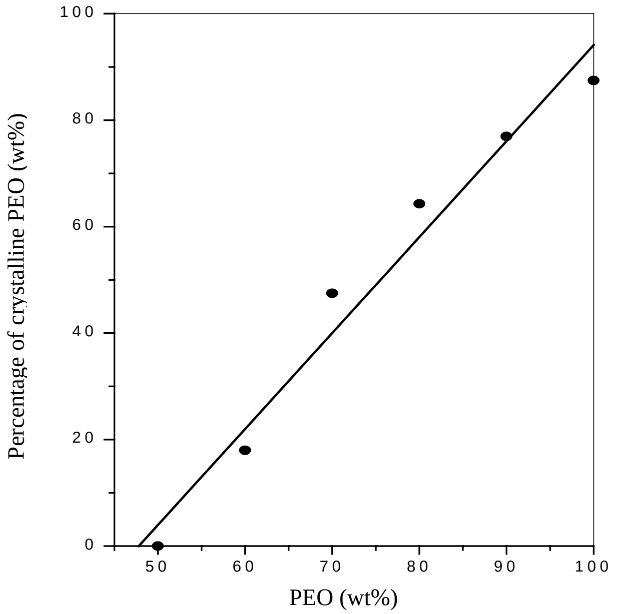

Fig. 2. The weight percentage of crystalline PEO vs. PEO concentration on PEO/PTMPTMA interpenetrate networks system.

calculated from the following relation:

$$C_r = \frac{\Delta H_f}{\chi_A \times \Delta H_f^0} \times 100\%, \qquad (1)$$

where ΔH_f is the apparent heat of fusion per gram of the samples, χ_A is the concentration of PEO in wt% in the interpenetrate networks and ΔH_f^0 is the thermodynamic heat of fusion per gram of completely crystalline PEO [39]. The amount of crystallizable PEO in the PEO/PTMPTMA interpenetrate networks is reduced with the increase of PTMPTMA, as shown in Fig. 2. PEO is not able to crystallize when the PEO concentration is lower than 50 wt%. The weight percentage of crystalline PEO in the composites almost forms a straight line when it is plotted against PEO wt%. We have also investigated the crystallization behavior of PEO in inorganic networks [40], which were prepared by a sol–gel process, and found to have the same trend as shown in Fig. 2. From the experimental process we knew that the PEO here crystallized from the molten state, and the DSC studies indicate that the reduction in weight percentage of crystalline PEO results from the confined movement of macromolecular chains in the PTMPTMA networks. At the low weight percentage of PEO in the interpenetrate networks, PEO is thoroughly interpenetrated in the PTMPTMA networks, the movement of macromolecular chains is limited by the PTMPTMA net, and hence it is difficult to crystallize. On the contrary, at the higher weight percentage of PEO in this system, the network is not perfect and the net-density is low, so a part of the polymer is out of the networks and becomes crystalline phase in the interpenetrate networks. Fig. 3 shows the DSC result of the melting points and crystallizing temperature of PEO in the PEO/PTMPTMA interpenetrate net, when the PEO can crystallize in the networks corresponding to the concentration of PEO wt%. The melting temperature T_m was taken as the temperature corresponding to the maximum of the melting peak when the samples were heated from 0 to 100°C, and the crystalline temperature T_c was taken as the temperature corresponding to the minimum of the exothermic peak due to crystallization when the samples were cooled from 100 to 0°C. The melting points of PEO in the networks are lower than that of pure PEO, as shown in Fig. 3. We can infer that the crystalline phase of confined PEO would be different from the crystalline phase of pure PEO, block copolymers and that of blending with other polymers, and that the crystalline morphology of PEO in the averaging degree of confined environment will be different. This phenomenon is also different from the melting of PEO in silica networks. When PEO was in silica networks, the melting points of different concentrations are almost the same. The reason being that PTMPTMA networks are softer than silica networks, and PEO can crystallize into different sizes of lamella with altered PEO concentration in the samples.

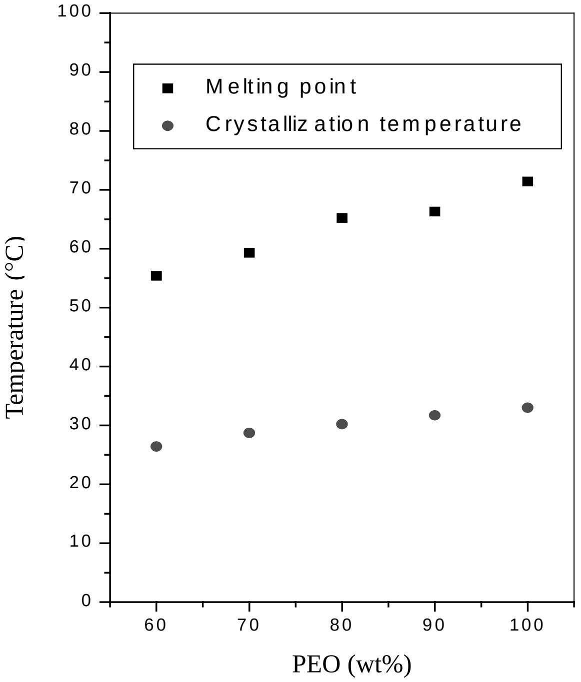

Fig. 3. Melting point and crystallization temperature of PEO in PEO/PTMPTMA interpenetrate networks vs. PEO wt%.

Fig. 4 shows the scanning electron micrographs of PEO/PTMPTMA interpenetrated network fracture surfaces at 50, 60, 70, and 90 wt% PEO. The micrographs in Fig. 4 show that the increase in the amount of PEO used in the samples causes an increase in dimensions of the domains due to the separation of the polymer phase. PEO/PTMPTMA interpenetrate networks with a weight ratio of 1:1 has no clear PEO

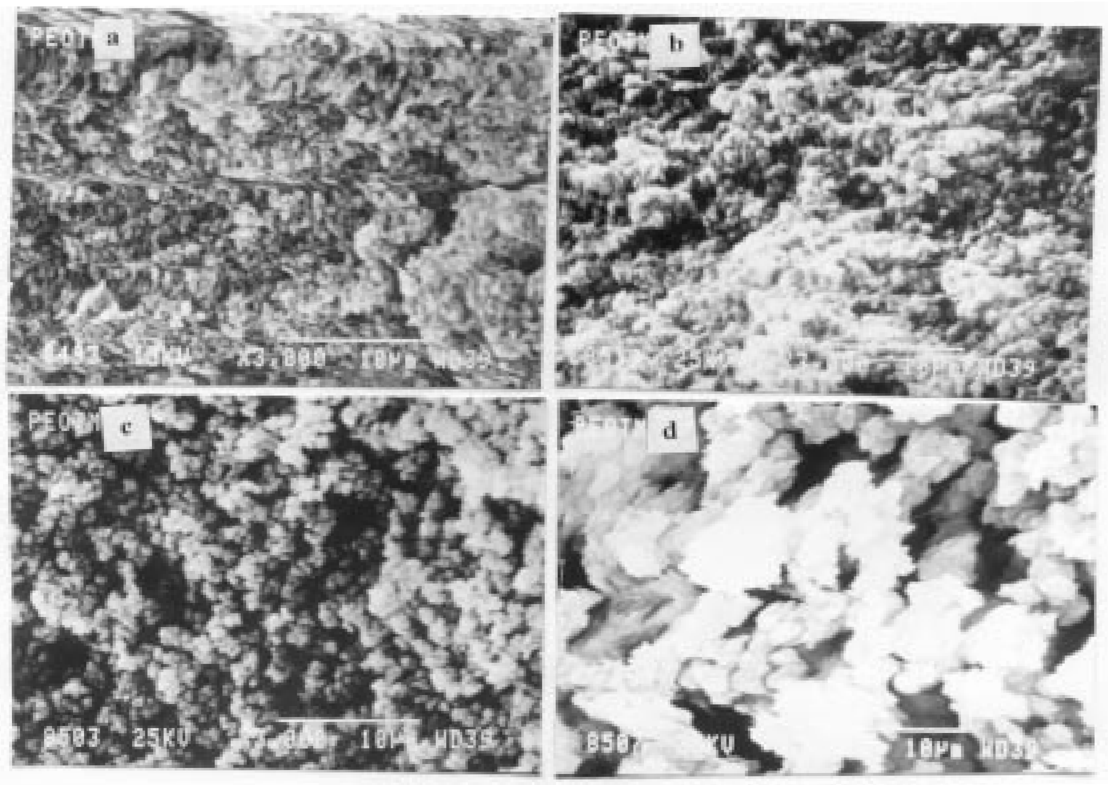

Fig. 4. SEM photographs of the fracture surface of PEO/PTMPTMA interpenetrate networks: (a) 50 wt% PEO, (b) 60% wt% PEO, (c) 70 wt% PEO, and (d) 90 wt% PEO.

phase. It agrees with the DSC and WAXD results well, and it seems reasonable to conclude that the movement of the PEO molecular chains is highly confined in the PTMPTMA networks, and that PEO cannot crystallize in these networks. Fig. 4(b)–(d) show that the PEO phase becomes larger and larger with the increase of PEO amount in the interpenetrate networks, and this means that PEO still crystallizes when it is out of the networks.

Fig. 5 shows SEM photographs of the fracture surface of PEO/PTMPTMA interpenetrate networks after PEO being extracted by $CHCl_3$. The morphology of PTMPTMA networks becomes gradually finer and finer with increasing PTMPTMA contents in the interpenetrate networks system. The density of the networks was also influenced by the increase of PEO.

Fig. 6 shows the WAXD reflection patterns of the same samples as in Fig. 1. The DSC result showed that PEO could not crystallize in the networks system when the PEO weight ratio is lower than 50%, and its crystallinity reduces with the increase of PTMPTMA weight ratio while the PEO weight ratio is higher than 60%. The WAXD patterns in Fig. 6 correspond well to this result. But the crystal structure of PEO in PTMPTMA networks has not changed. The crystallite size perpendicular to the (*hkl*) plane, L_{hkl} in nm, is usually given by the Scherrer equation [41]:

$$L_{hkl} = \frac{K\lambda}{\beta \cos\theta}, \tag{2}$$

where K is the Scherrer shape factor, here $K = 0.9$, λ is the wavelength of X-ray, θ is the Bragg angle, β is the pure line broadening, B is the measured half-width of the experiment profile (in degrees); and b_0 is the instrumental broadening, which was obtained to be 0.15° from scans of standard silicon power. Using the above definitions of β, B and b_0 and assuming peak shapes to be gaussian, $\beta = (B^2 - b_0^2)$. As an example, the values of the crystallite size perpendicular to (120) plane L_{120} at several selected ratios are presented in Table 1. It shows that L_{120} increases not as much as PEO in silica networks with increasing PEO wt%. The cause of such

Table 1
Crystalline size of L_{120} of PEO in PEO/PTMPTMA interpenetrate networks with different PEO content

PEO (wt%)	$2\theta^a$	B^b	β^c	L_{120} (nm)
100	19.09	0.83	0.816	9.87
90	19.04	0.84	0.826	9.75
80	19.01	1.02	1.001	8.04
70	19.19	1.03	1.019	7.90
60	19.11	1.21	1.201	6.71

[a] Bragg angle.

[b] Measured half-width of the experimental profile (in degree).

[c] Pure line broadening (in degree).

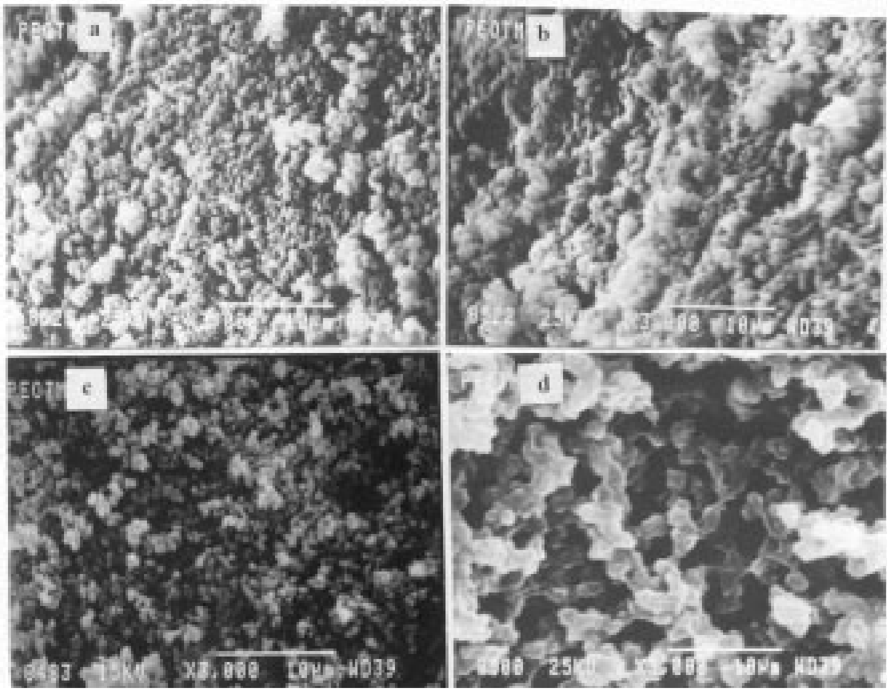

Fig. 5. SEM photographs of the fracture surface of PEO/PTMPTMA interpenetrate networks after being extracted by $CHCl_3$: (a) 50 wt% PEO, (b) 60% wt% PEO, (c) 70 wt% PEO, and (d) 90 wt% PEO.

a phenomenon is probably that the nucleation process of the PEO crystallization was strictly confined by the PTMPTMA networks.

According to the DSC, SEM and WAXD results, we assume that PEO in one sample is composed of two parts, one part is an unperturbed PEO, the other part is a confined PEO, and the confined PEO is equal to PTMPTMA in weight percentage. On the basis of the hypothesis that PEO cannot crystallize when the sample composed of 50 wt% PEO and 50 wt% PTMPTMA, we can analyse the crystallization behavior of PEO in the interpenetrated network system. At the low (under 50 wt%) weight percentage PEO, the PEO chain is thoroughly in the PTMPTMA network and its movement is strictly confined by the network; at the high (over 50 wt%) weight percentage, part of PEO is in an unperturbed state, so it can crystallize and the crystalline PEO has the same melting point and the same crystalline structure. All of the unperturbed PEO is in a confined space, so its crystallinity and melting temperature are different from the pure PEO. Thus, we can calculate the crystallinity of an unperturbed PEO in a PEO/PTMPTMA interpenetrated network system from the following equation:

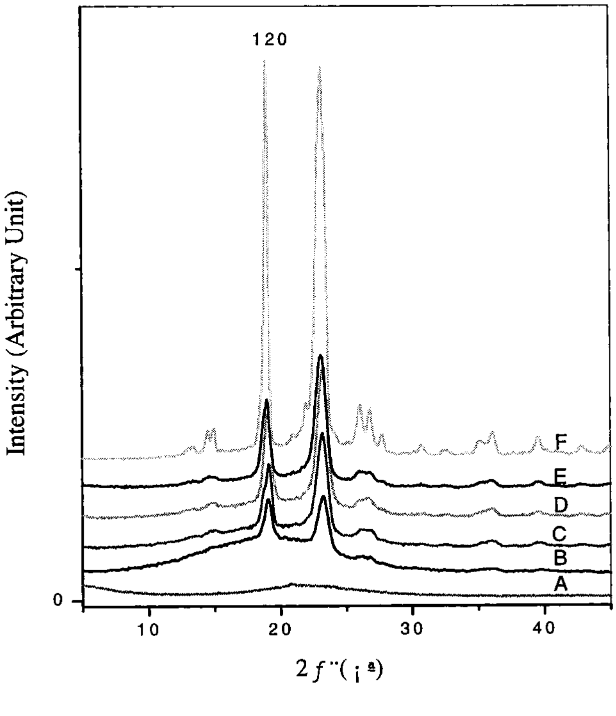

Fig. 6. WAXD patterns for PEO/PTMPTMA interpenetrate networks with different weight ratios (A: 50 wt% PEO, B: 60 wt% PEO, C: 70 wt% PEO, D: 80 wt% EPO, E: 90 wt% PEO, and F: pure PEO).

$$C'_r = \frac{\Delta H_f}{\left(\left(1 - \frac{1 - x_A}{1 - n}\right)\Delta H'_f\right) \times 100\%}, \tag{3}$$

where C'_r is the crystallinity of the unperturbed PEO in the sample, ΔH_f is the apparent heat of fusion per gram of the sample, x_A is the concentration of PEO wt% in the materials, n is the concentration of PEO when PEO is uncrystallizable in the samples (here $n = 50\%$), and $\Delta H'_f$ is the apparent heat of fusion per gram of pure PEO. The calculated result is

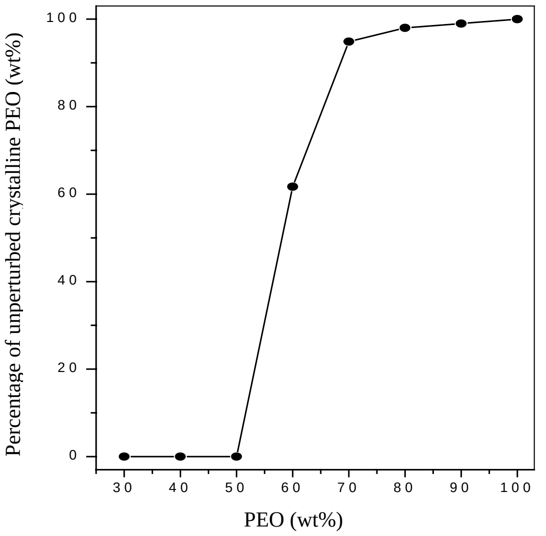

Fig. 7. The weight percentage of unperturbed crystalline PEO vs. PEO concentration in PEO/PTMPTMA interpenetrate networks system.

shown in Fig. 7. There is an obvious transition of C_r' in this system. The PEO crystallinity did not change very much from 70 to 90 wt% in this system, but when the PEO weight percentage is lower than 70 wt% in the PEO/PTMPTMA interpenetrated network system, there is a mutation of C_r'. This indicates that there must be a transition structure of the samples as shown in the SEM photographs. The percolation theory was found to be a good model for this phenomenon [42,43].

4. Conclusions

The present study of PEO/PTMPTMA interpenetrate networks enables us to understand the behavior of PEO in confined environments better. PEO in the networks is not able to crystallize at weight ratio that is lower than 50%. Crystalline PEO in the PTMPTMA networks has a melting temperature different from the PEO in silica networks. The melting temperature of crystalline PEO in the interpenetrate networks system is lower than that of pure PEO. The movement of a PEO molecular chain in the PEO/PTMPTMA interpenetrate networks system can be strictly confined by the PTMPTMA networks and the networks are also affected by PEO in this system. The calculations of unperturbed crystallinity of PEO in the networks show that the percolation theory was found to be a good model for this system.

Acknowledgements

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