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Swollen interpenetrating polymer networks

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Abstract

The swelling in common (benzene) and selective (CCl_4) solvents and small angle X-ray scattering (SAXS) of interpenetrating polymer networks (IPNs) of PPO/PMMA in all composition intervals are studied. It is shown that in both solvents IPNs swell better than the pure crosslinked polymers; that may be caused by a smaller degree of crosslinking of each component in IPN in comparison with the crosslinking of pure polymers. This leads to lower network density in IPNs than in the networks of pure polymers. The unusual effect is found: the IPN enriched with PMMA has the maximum swelling in CCl_4, whereas PMMA itself does not swell in this solvent. SAXS measurements show that ordering in IPNs, i.e. microphase separation (MPS), is absent, but there are structural heterogeneities in the initial dry state of IPNs which are typical for these systems. These heterogeneities grow after swelling in a selective solvent. We suggest that PMMA units cluster together in poor solvent and as a result the internal stresses arise during swelling, which causes the large swelling of IPNs in selective solvent. The structure of the asymmetrical IPNs does not change with temperatures increasing up to 95°C and dropping down to room temperature; as a consequence, the equilibrium swelling is also insensitive to the temperature. On the contrary, the structure of symmetrical IPNs changes with heating and comes back very slowly by returning to room temperature. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Interpenetrating Polymer Networks (IPN) is a very interesting class of polymer systems [1,2] whose properties change either monotonically or nonmonotonically with the change of the ratio of crosslinked monomers or polymers. As a rule, IPNs are microheterogeneous systems because of the incompatibility between components that causes microphase separation. The entanglements between dissimilar macromolecules prevent the complete separation, and only microphase separation (MPS) occurs.

Contrary to most of the IPNs described in the literature, which are microheterogenous in the initial state [3,4], the IPNs synthesized by Frisch et al. are often homogeneous, which is confirmed by having a single glass transition temperature of the system [5]. The homogeneity is achieved by choosing a kinetic regime in such a way that crosslinking occurs faster than microphase separation [6]. Such an idealized case is considered theoretically in Ref. [7]. However, some authors [8,9] had doubt in the experimental realization of one-phase IPNs.

In the series of recent papers Schulz and Frisch considered swollen gels of IPNs with special attention paid to the role of the nature of the solvent in the MPS in these gels [10,11]. The purpose of this work is the experimental evaluation of the ordering in the initial IPNs and the change of this process and structure parameters as a result of the swelling of IPNs in common and selective solvents. In general our experiments confirm many of the conclusions in Ref. [11].

2. Experimental

As a suitable example of an IPN we have chosen the IPN of PPO and PMMA with the composition ratios PPO/PMMA 70/30, 50/50, 30/70, 20/80. The preparation of these IPNs is described in Ref. [12]. The microstructure of the IPNs was measured by (SAXS) on a small X-ray diffractometer AMUR-K with a Kratki-collimator and a linear position-sensitive detector. Cu-anode X-ray fine focus tube (30 kV, 30 mA) was employed as a source of the X-ray radiation. This diffractometer was made in the Institute of Crystallography of the Russian Academy of Sciences [13]. The linear position-sensitive detector was produced in the Institute of Nuclear Physics, Siberian Department of the Russian Academy of Sciences [14].

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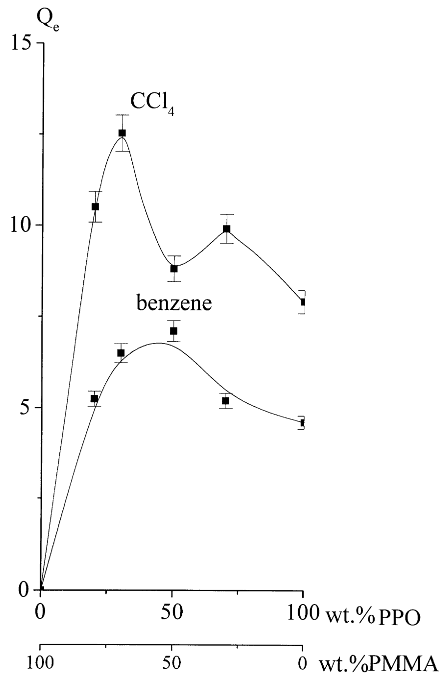

Fig. 1. Swelling of IPNs of different composition in CCl_4 and benzene.

This detector has a window of 10 mm × 100 mm arranged in a vertical plane. The linear resolution of the detector is 0.3 mm. The monochromatization is achieved with graphite monochromator. The registration system of the detector is made with a CAMAC standard and is connected to a PC computer. The exposure time was 1000 s. The corrections to the intensity of X-ray beam and the absorption coefficient evaluation was made. The smoothing, the subtraction of background and the input of the collimation corrections were carried out at the end. The calculation programs for these operations were developed in the small-angle scattering laboratory of the Institute of Crystallography of the Russian Academy of Sciences [15–18].

The swelling of the IPNs was measured in the laboratory of Polymer Physics of the Institute of Organoelement Compounds of the Russian Academy of Sciences, by a gravimetric method. As a rule the measurements were carried out at 25°C, but some experiments were performed at temperatures of 52 and 73°C for comparison. Two–four parallel measurements were carried out for every system studied: the difference between them was 4–7%. The solvents were removed from the sample surface by filter paper before weighting. The degree of swelling Q is the ratio of the weights of swollen to dry sample. Q_e is the equilibrium degree of swelling.

3. Results and discussion

3.1. Swelling of IPNs

Preliminary experiments showed that equilibrium degree of swelling is achieved during 5–8 days at 25°C and 5 h at 52 and 73°C. This why every sample was swollen at 25°C for 8 days.

The screening of the solvents was carried out, and showed that:

1. Benzene, dioxane, DMSO, chlorobenzene are common solvents for both polymers, but PPO always swells more than PMMA (for example, Q_e of PPO in benzene is 400% and Q_e of PMMA is only 120%).
2. CCl_4 is a nonsolvent for PMMA and a good solvent for PPO (better than the above mentioned solvents).
3. Petroleum ether and cyclohexane are common nonsolvents for both polymers. The latter means that one can expect the macroscopic volume transition (collapse) of IPNs at some critical amount of nonsolvent in a mixture with a common solvent, as is known in the literature for gels of homopolymers [19,20]. However, as we will see below, swelling decreases very gradually as the system is being enriched with nonsolvent.

Fig. 1 shows the dependence of swelling of the IPN on its composition in two solvents: benzene and CCl_4. The highly swollen samples of IPNs are gels, but as the initial samples are composed of films rather than cylinders, they lose their integrity and it is not possible to evaluate the change in their mechanical properties. The samples, whose degree of swelling is smaller than 5–7, are not gels; they are only swollen films. It is worth noting that gels and swollen films do not lose the total solvent during drying, and the second degree of swelling is always lower than the first one.

Several characteristic features should be noted in swelling of the IPNs:

1. Similar to the previous results of two of the authors on the swelling of the IPN PCU/PMMA (polycarbonate urethane/polymethylmethacrylate) [21], the IPN PPO/PMMA also swells in both solvents more than pure crosslinked polymers. It may therefore be deduced that this is a typical behavior of IPNs, which is caused by a smaller degree of crosslinking of the components of the IPNs than the one of pure polymers and by the lower density of the network in the IPNs.
2. Maximum swelling is achieved in good solvents at symmetrical compositions of the IPN. In a selective solvent the IPN of this composition is characterized by minimum swelling. This behavior corresponds to the theoretical prediction of Schulz and Frisch [11].
3. The more striking phenomenon of the maximum degree of swelling of the IPN enriched in PMMA (PPO/PMMA 30/70) was discovered in CCl_4 that does not dissolve PMMA. The reason for this behavior can be partially understood from the results of the structural study of this IPN, as we show later.

The IPN PPO/PMMA 20/80 demonstrates very strange behavior. It does not swell but kind of dissolves in benzene and in mixtures of benzene/CCl_4 up to 50% of CCl_4. The

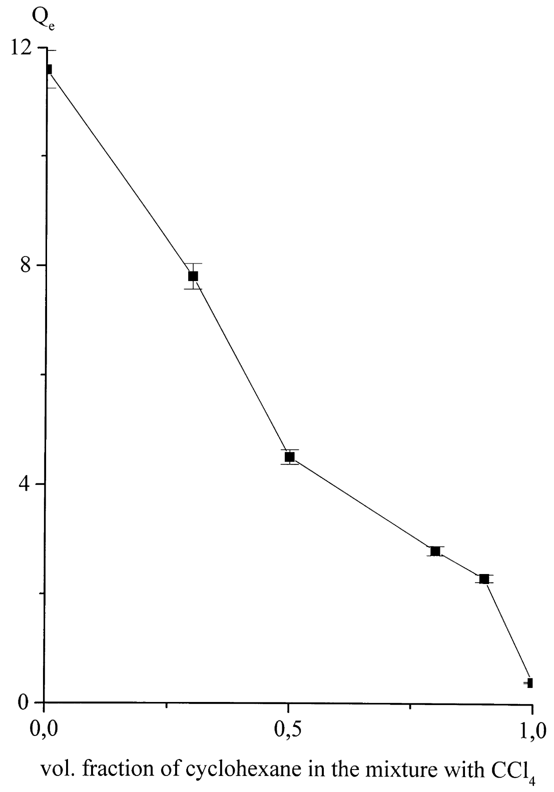

Fig. 2. Decrease of equilibrium swelling of the IPN containing 70% PPO at the transition from good solvent, CCl_4, to the common nonsolvent, cyclohexane.

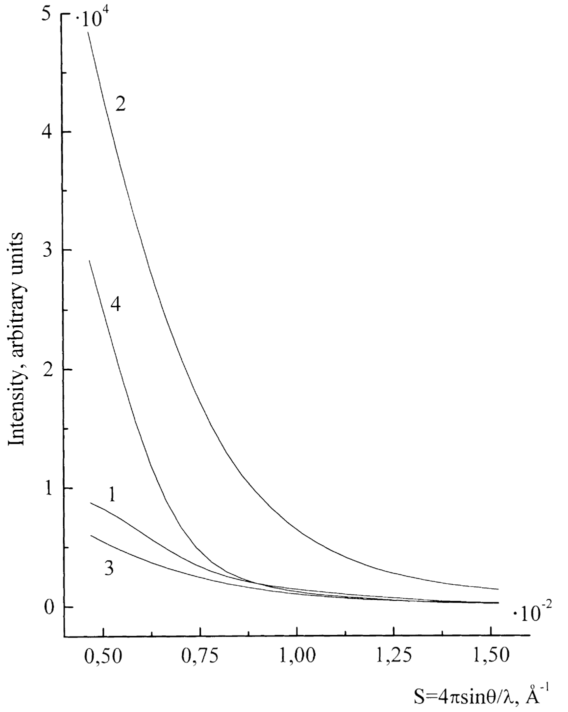

Fig. 3. SAXS curves of the IPNs PPO/PMAA 30/70 (1 and 2) and 70/30 (3 and 4) in initial state (1 and 3) and after equilibrium swelling in CCl_4 and following the removal of the solvent under a vacuum 10^{-2} Hg for 5 days (2 and 4).

reason for such a behavior can be the screening of the PMMA repeat units in the PMMA-rich regions by PPO. At greater amounts of CCl_4 and in CCl_4 itself this IPN and pure PMMA neither dissolve nor swell, but IPN of this composition crack into small pieces. This is probably due to Case II Diffusion [22]. Maybe this network is very imperfect as a consequence of the difficulties of crosslinking the mixture containing 80% PMMA, and as a result it may “dissolve” in a good solvent.

The increase in swelling temperature of the samples PPO/PMAA 70/30 and 30/70 leads only to increase in the speed of swelling (the equilibrium is achieved in 5 h instead of 5–8 days) but the equilibrium value is independent of the temperature. As we will show below, this correlates with SAXS results demonstrating that scattering curves of the IPNs of these compositions do not depend on temperature.

Fig. 2 shows the gradual decrease of IPN swelling when transition is made from CCl_4 to a common nonsolvent—cyclohexane; no jump-like volume transition is observed. According to Ref. [11] such behavior can be realized if the osmotic pressure is sufficiently high in comparison with the critical pressure.

3.2. SAXS measurements

Fig. 3 shows the X-ray scattering curves (in arbitrary units) of IPNs PPO/PMMA 70/30 and 30/70 in the initial dry state, and in the state when equilibrium swelling in CCl_4 was reached and the solvent was removed under vacuum 10^{-2} Hg at a temperature 70°C for 5 days. The scattering vector $S = 4\pi \sin \theta/\lambda$ ($\lambda = 0.1542$ nm is the wavelength, θ is a half of the scattering angle) is plotted on the x-axis.

The measurement of swollen samples scattering is impossible due to large absorption by the solvent. However, it is known from the example of block-copolymers that the structural changes taking place during swelling in selective solvents are kept after removing this solvent [23].

The scattering curves of the asymmetrical IPNs do not change after heating both samples up to 95°C and cooling them back to 23°C. This means the structure of these samples is not dependent on the temperature causing their equilibrium swelling not being dependent on the temperature as well. At the same time the scattering from the IPN of symmetrical composition increases with the temperature, which is shown in Fig. 4. The scattering curves take a long time to return to the initial state after cooling.

The question arises: what is the character of the structures scattering the X-rays at small angles? It is shown in Figs. 3 and 4 that there is no maximum on the scattering curves of all samples and at all temperatures studied. This points to the absence of ordering or microphase separation (MPS) in the IPNs in their initial state and after swelling in selective solvents. However, these systems are not homogeneous: the scattering exists only at the smallest angles, which is caused by the fluctuations of electronic density of the size of several

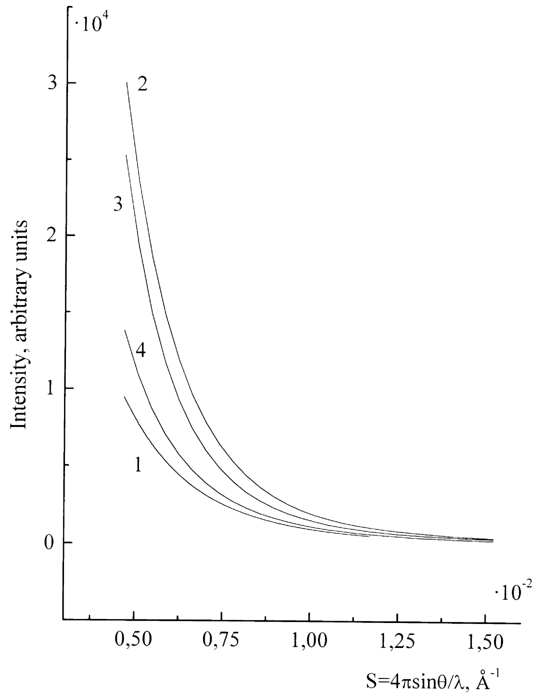

Fig. 4. SAXS curves of the IPN of symmetrical composition (PPO/PMMA 50/50) in the initial dry state at 23°C (1), then heated to 95°C (2) and cooled to 23°C for 2 (3) and 15 (4) h.

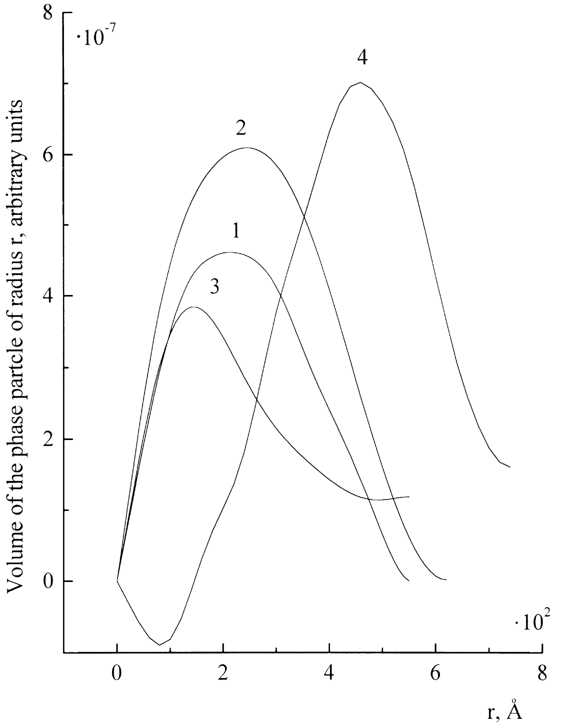

Fig. 5. Volume size distribution in the samples of the IPN containing 70 (1) and 30% (3) PPO in the initial dry state, and in the same samples after equilibrium swelling in CCl_4 and then removal of the solvent under vacuum (2 and 4, respectively).

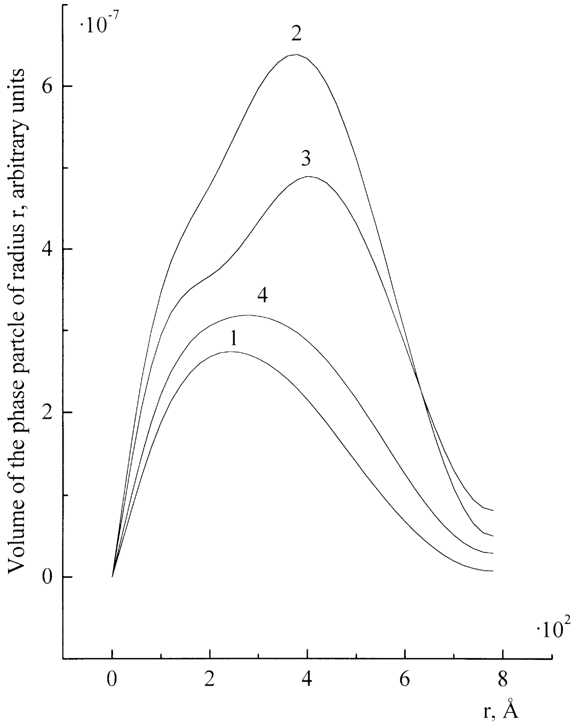

Fig. 6. Volume size distribution in the symmetrical IPN in the initial state at 23°C (1), then heated to 95°C (2) and cooled to 23°C for 2 (3) and 15 (4) h.

dozens nm (15–40 nm). Close values of fluctuations were found in Ref. [24] for IPNs PCU/PMMA.

We have calculated the size distributions of these structural inhomogeneities. Because it is difficult to imagine that the system is monodisperse and we have no data about the shape of these inhomogeneities, we have calculated an equivalent volume distribution function of hard spheres, which is the most general characteristic in such cases, according to the method developed in Ref. [15]. These distributions are shown in Figs. 5 and 6. On the *y*-axis are plotted the volume fractions of spheres having the radius plotted on the *x*-axis.

It is interesting to compare the results of both the experimental methods used. The presence of the inhomogeneities is a typical result of the IPN formation. Thus, according to Refs. [24,25], the IPN is composed of PPO (A)-rich and PMMA (B)-rich phases of nm-scales. A B-rich phase means that the concentration of component B is larger than the average. It can be expected that IPNs with a large amount of PPO is controlled only by PPO. In other words, the PMMA repeat units in the PMMA-rich phases are screened by PPO repeat units. Thus, the maximum swelling is obtained for a composition ratio close to 100% PPO (in Fig. 1 it is 70% PPO). A higher amount of PMMA leads to a reduction of the swelling parameters. But further increasing the PMMA stops screening of the PMMA in the PMMA-rich inhomogeneities. The PMMA collapses to smaller clusters and the remaining PPO is no longer screened by the PMMA monomers. Thus the second swelling can be observed (30% PPO).

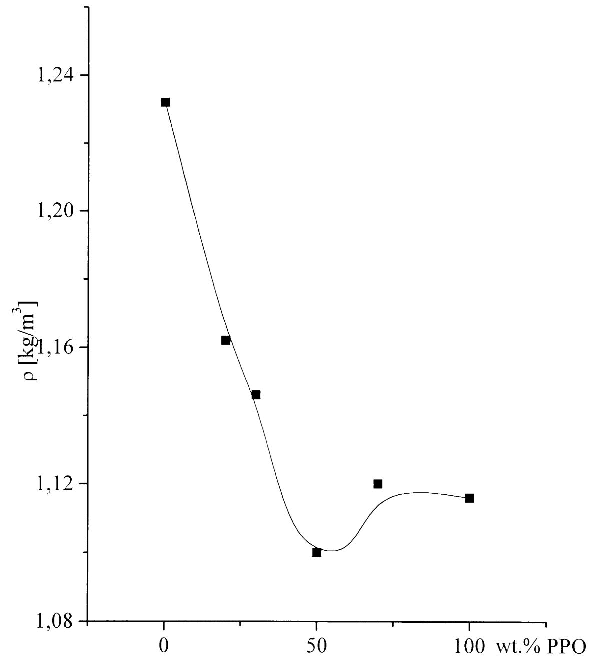

Fig. 7. Dependence of the IPN density on the composition.

One can see that for all IPN compositions the size of the sphere increases after swelling or raising the temperature. The most interesting fact is that (see Fig. 5) the structure of the sample enriched in PPO changes only slightly during swelling (the distribution maximum displaces negligibly—from 20 to 25 nm); the structure of the sample enriched in PMMA, on the contrary, changes dramatically after swelling in the nonsolvent for PMMA, namely from 15 to 45 nm. We believe that in this sample the fragments of PMMA chains gather together, forming the clusters, and the presence of these large particles creates internal stresses that cause the abnormally large swelling of this IPN in the selective solvent.

The structure of both these IPNs is not sensitive to the temperature. On the contrary, the structure of symmetrical IPN (PPO/PMMA 50/50) in the dry state changes considerably with temperature, as is seen in Fig. 6. The size of fluctuations increases after heating the sample up to 95° and gradually decreases with cooling, but this change is not reversible and at room temperature the size is slightly larger than prior heating.

Behavior of symmetrical IPN distinguishes from IPNs of other compositions in several aspects. Thus, the density of this IPN has a minimal value, as shown below. This can be the result of different structural factors of these IPNs, proposed by two of the authors in Ref. [11].

3.3. Density

Dependence of the density of IPNs on their composition is shown in Fig. 7. It changes only a little as compared with pure PPO on enriching the system with PMMA up to 50%. This composition is characterized by minimum ρ and with further increase of PMMA content ρ grows sharply. This correlates with the other data showing that the microstructure of the IPN in the interval of 50–100% PMMA changes considerably in comparison with the IPNs having a smaller content of PMMA.

4. Conclusion

The study of swelling of the IPNs PPO/PMMA in common and selective solvents and the measurement of their structure by SAXS has shown that microphase separation is absent in these IPNs in the initial dry state. These systems are, however, not homogeneous since the scattering occurs only at the smallest angles. The distribution of structural heterogeneities is calculated by a special program. In the PMMA-rich regions the PMMA monomers are screened by PPO and this can cause the solubility of such a sample in benzene. The structure and equilibrium swelling of IPNs containing 30 and 70% of PPO are not sensitive to temperature changes, whereas at symmetrical composition of the IPN the scattering increases with the temperature rise and this increase is not reversible.

The structure elements grow with swelling, especially in selective solvents. In good solvent maximum swelling is achieved at symmetrical composition of the IPN, and in selective solvent this composition is characterized by minimum swelling. We suggest that the fragments of PMMA chains gather together in CCl_4, which is nonsolvent for PMMA. These clusters give rise to internal stresses and that is the reason for the maximum swelling of PMMA enriched IPNs in this selective solvent.

Acknowledgements

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