

Microphase structure features of network block polymer over a wide temperature range

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Changes in the microheterogeneous structure of a network block polymer based on diene and epoxy blocks have been studied using the small-angle X-ray scattering technique with a position sensitive detector. The formation of a three-dimensional chemical bond network is shown to result in microphase separation of chemically distinct blocks. The resulting microphase structure is stabilized by the three-dimensional network which prevents the establishment of a thermodynamic equilibrium in the system over a wide temperature range.

Keywords Position sensitive counter; network block polymer; temperature changes of microheterogeneous structure; small-angle X-ray scattering

INTRODUCTION

Early quantitative small-angle X-ray scattering investigations of a phase state of network block polymers gave the evidence of chemically-distinct-block microphase separation under certain conditions^{1,2}. Up to now there has been no consideration of similar systems in the framework of phase diagram formalism; that is from considerations of thermodynamic stability of either the single- or two-phase state, primarily because there are usually no data on the phase equilibrium in mixtures of chemically unbonded blocks. Therefore, in most cases it is not known in which region of the phase diagram the system might be prior to curing and in the course of curing. Further, a diffraction experimental procedure in a temperature range as wide as possible, covering both one- and two-phase regions of the phase diagram, involves prolonged heat treatment and, therefore, irreversible changes in the polymer chemical structure can occur. Thus, these experiments are not sufficiently expedient when use is made of a conventional small-angle experimental technique which requires long exposure time for recording the scattering curve in the necessary angle interval. The apparatus which allows similar experiments to be carried out in a few minutes has only recently become available³⁻⁵.

EXPERIMENTAL

A polymer based on diene and epoxy blocks was chosen for the study of changes in microphase structure in a wide temperature range. Similar systems are known to have pronounced microphase structure⁶. Oligoisoprendihydrazide of molecular mass 3100, with 3.75% content of

hydrazide groups, and diglycidyl ether of bisphenyl (molecular mass, 342; content of epoxy groups, 25.3%; melting point, 42–43°C) are the initial components of the polymer. The process used to produce this polymer has been described in detail elsewhere⁷. For structural investigations, films of 2 mm thickness, obtained at equivalent ratios of the components (18 wt% of epoxy oligomere), were used. The system curing time was 10 h at 110°C. The chemical cure occurs before the SAXS temperature scans are carried out.

Small-angle X-ray scattering curves were obtained using a high-temperature small-angle diffractometer developed in Institute of Metals Physics, Academy of Sciences of the Ukr.SSR (Figure 1). The primary beam

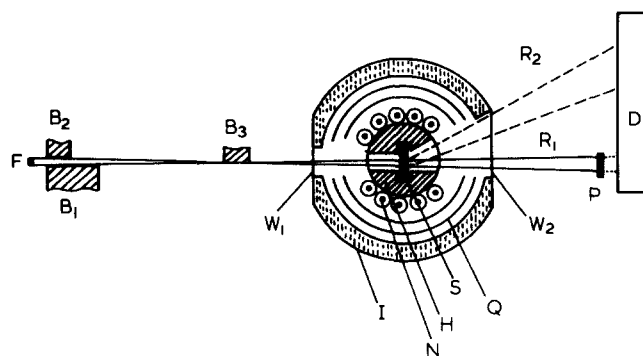


Figure 1 Small-angle diffractometer: F, the focal spot of the X-ray tube; B₁, B₂, B₃, the Kratky collimator; S, a sample under study; R₁, R₂, the primary beam and scattered X-ray radiation; P, the primary beam stopper; H, a sample holder block; N, a heater; Q, thermal screens; I, water-cooled housing; W₁, W₂, windows for the primary beam and scattered radiation; D, a positive sensitive detector

collimation is carried out following the procedure of Kratky⁸. The temperature chamber allows a sample to be thermostated in a vacuum or in an inert gas. The entire volume of the apparatus in the path of the primary beam, from the entrance slit of the collimator up to the detector window, is evacuated. Sample heating and thermostating is carried out by a serial heat setting system. Radiation scattered by a sample is registered using a position sensitive detector (D, Figure 1). With the sample-registration plane distance being 600 mm and the detector linear resolution 0.11 mm, the angular detector resolution is 0.0105°. Pulses registered by the detector are stored in the on-line memory of a multi-channel analyser PA-1024. The total number of analyser channels can be divided into several equivalent groups which allows the exposure time to be changed depending on the form of the small-angle scattering curve so that the scattered intensity value for each point of the curve is obtained with a given degree of accuracy.

Chromium anode radiation with a vanadium filter in the primary beam is used. The sample temperature ranges from 20 to 270°C. The exposure time for obtaining a small-angle diffraction pattern is equal to 10 min. For the geometry used this allowed at least 1000 pulses to be stored in each analyser channel, i.e. for each point of the scattering curve. The curves are processed by subtracting background chamber scattering from the primary data to give the X-ray absorption of the sample.

EXPERIMENTAL RESULTS AND DISCUSSION

Small-angle X-ray scattering curves obtained at various temperatures are shown in Figure 2. Curves corresponding to the temperature interval 20°–260°C exhibit a well-defined diffraction maxima the position of which slightly shifts with temperature to lesser scattering angles. All the curves have a common crossover point corresponding to the Bragg periodicity 4.8 nm. A temperature increase up to 270°C considerably changes the angular distribution of the intensity. In this case the total scattering level

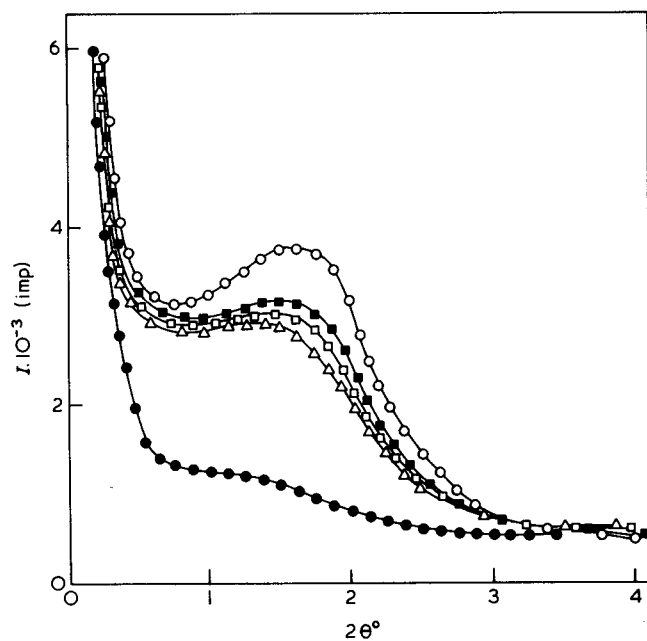


Figure 2 Small-angle X-ray scattering curves for network polymer obtained at various temperatures: ○, 20; ■, 190; □, 217; △, 260; ●, 270°C

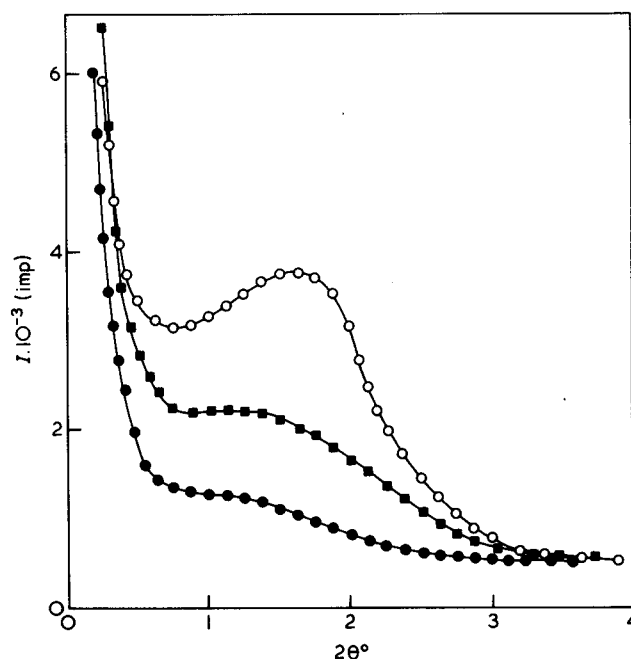


Figure 3 Small-angle X-ray scattering curves for initial network polymer at 20°C (○), 270°C (●), and for a sample studied at temperatures 190, 217, 260 and 270°C, and cooled to 20°C (■)

decreases substantially and a diffraction maximum becomes hardly observable against a diffuse halo. The scattering curve for this temperature does not pass through the intersection of the remainder.

Figure 3 presents a small-angle scattering curve of a sample after being heat treated at temperatures 190, 217, 260 and 270°C and then cooled to ambient temperature. Because of interest in comparing this curve with those at initial (20°C) and maximum attainable (270°C) temperatures both of these curves are also shown in Figure 3. It is noteworthy that scattering curves of the initial and a heat treated sample obtained at room temperature differ whereas the curves of a heat-treated sample and that at 270°C exhibit similar intensity distributions.

Figure 4 shows temperature dependences of (a) Bragg periodicity corresponding to a small-angle diffraction maximum; (b) intensity of the maximum; and (c) the so-called small-angle X-ray scattering invariant⁹ which is a measure of the system turbidity in the X-ray region. Temperature increase from 20° to 260°C results in a 15% increase of the Bragg periodicity. However, a further increase in temperature of only 10°C results in the periodicity increasing by 10%, i.e. the period thermal expansion coefficient in the temperature range 260°–270°C is an order of magnitude higher than that in the range 20–260°C. Cooling of the sample from 270° to 20°C does not change the Bragg periodicity.

Temperature increase from 20 to 260°C results in an approximately rectilinear decrease in the small-angle maximum intensity and small-angle X-ray scattering invariant value. Further increase of temperature up to 270°C causes abrupt changes in these characteristics. Cooling to room temperature leads to increase in the small-angle maximum intensity and small-angle X-ray scattering invariant but their magnitude does not attain that of the initial sample. Thus, abrupt changes in small-angle scattering profiles and corresponding characteristics of heterogeneous structure occur during heating to

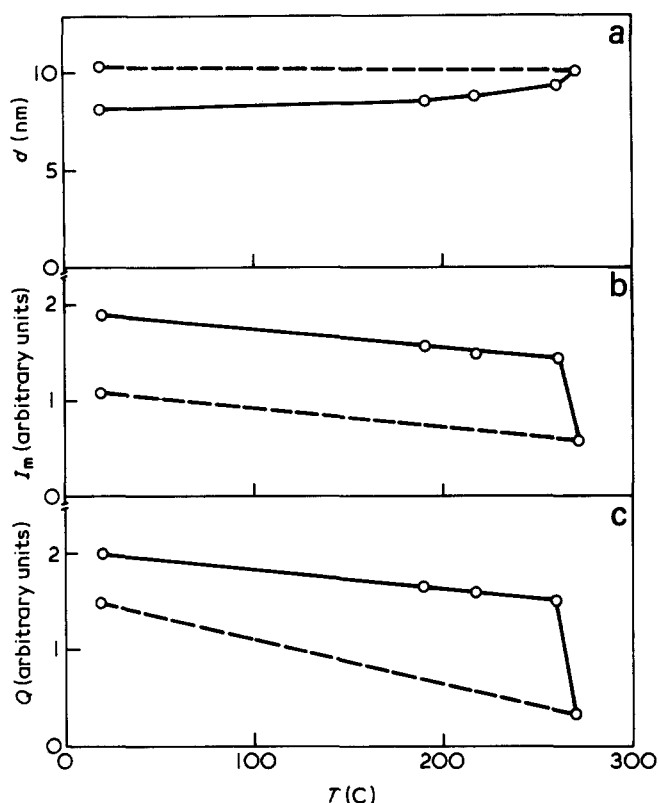


Figure 4 (a) Temperature dependences of Bragg periodicity; (b) discrete small-angle maximum intensity; and (c) small-angle X-ray scattering invariant for the network polymer

temperatures exceeding 260°C. In the temperature range 20–260°C these characteristics change to a large extent reversibly. Reversibility of structural changes, however, no longer occurs following heating to temperatures > 260°C.

Using these data from the diffraction experiments it is useful to carry out a phase state analysis of the system under study prior to curing. A previous determination of turbidity points¹⁰ has shown that the phase diagram of the system is characterized by an upper critical solution temperature. With the initial reacting mixture containing 18 wt% of epoxy oligomer, phase separation occurs during cooling to 100°C. At 110°C both in visible and in X-ray ranges the initial system is transparent. Therefore, addition polymerization producing a network polymer proceeds in a one-phase system. However, due to the formation of the network polymer, which is optically transparent, the X-ray spectrum exhibits a considerable enhancement of the scattered intensity level. As has been shown previously⁶ the latter corresponds to the microphase separation of flexible and rigid blocks in these network polymers. The dimensions of the heterogeneous region, as inferred from the Bragg period, are ≈ 8 nm. Having resulted from block polymer formation the transition from a one- to a two-phase system is in contradiction with available theoretical concepts and experimental data^{11–13}. It follows from these papers that interblock chemical binding usually results in better compatibility in the system. The opposite tendency observed here may be due to the fact that the theories developed previously are applicable only to flexible block based systems and are unable to explain peculiarities in block polymers comprising flexible and rigid blocks.

Thus, the observed microphase separation is associated

with formation of an epoxy-diene polymer network structure and should be formally considered as resulting from compatibility failure of the flexible and rigid blocks. At the same time, the homogeneity of the system is maintained at a high level, exceeding the resolution of the small-angle camera (≈ 100 nm)¹⁰. It is particularly noteworthy that microphase separation of the system associated with a maximum on a small-angle X-ray scattering curve remains at temperatures considerably exceeding the binodal point of the initial system. This phenomenon is also unusual and requires a more complete analysis of the factors which produce it.

From the data obtained it follows that substantial and irreversible changes in the X-ray scattering patterns begin at 270°C. At this temperature, processes of network polymer destruction could begin to be significant. At the same time, changes in microphase structure resulting from temperature increase from 20 to 260°C have to be due to competition of two factors: decrease of the thermodynamic interaction parameter and microphase state stabilization by a three-dimensional network. For systems having an upper critical solution temperature the first factor is indicative of a tendency to a one-phase state as temperature increases.

A similar trend manifested as a reduction of intensity and a total disappearance of small-angle maxima with temperature has been observed for linear block polymers^{1,2}. In a number of cases a particular maximum shifts to the larger angles² but sometimes its position and corresponding Bragg periodicity remain unchanged¹.

It is known that in the unstable state region of the phase diagram time variations of a small-angle maximum intensity for a system decomposing according to the spinodal mechanism are described by an expression¹⁴:

$$I(s,t) = I(s,0) \exp[2R(s)t] \quad (1)$$

where t is time, $R(S)$ is an amplification factor with maximum value at $S = S_m$, S_m is a reciprocal space vector corresponding to position of a diffraction maximum.

Analogously to equation (1), it has been suggested that the temperature variations of a small-angle maximum are described by the relation¹:

$$I(s,\chi) = I(s,0) \exp[\alpha(s)\chi] \quad (2)$$

where $\alpha(s)$ is a factor with maximum value at $S = S_m$ which disappears at $S = S_c$, S_c corresponds to the crossover point of the relevant intensity curves at various temperatures, χ is a block interaction parameter which decreases with temperature. Roe¹ has shown that similar to $R(S)$ from equation (1), $\alpha(s)$ is expressed by

$$\alpha(s) = MS^2(-F'' + 2KS^2) \quad (3)$$

where F'' is a second derivative of the free energy with respect to concentration, M is a diffusion coefficient, K is a constant in an expression for the free energy concerned with a composition gradient and is dependent on the interaction between components.

If a block system is subject to the relation in equation (2) then the dependence of the intensity logarithm on the inverse temperature should be rectilinear. $\alpha(s)$ is determined by the slope of the corresponding curve.

It is noteworthy that the network polymer studied in the temperature range 20–260°C is characterized by

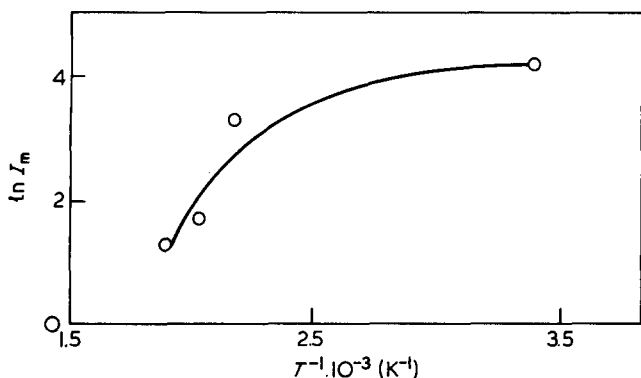


Figure 5 A plot of logarithm of small-angle maximum intensity versus inverse temperature

small-angle scattering curves which are similar to the corresponding family of curves observed during spinodal decomposition. An exterior feature of such a similarity is the occurrence of a tail-side intersection of the intensity curves concerned with various temperatures (crossover).

However, a more rigorous test is an examination of whether the small-angle scattering intensity is in agreement with the relation in equation (2). *Figure 5* shows the small-angle maximum intensity logarithm dependence on inverse temperature in the range 20°–260°C. It is evident that the dependence observed is significantly non-rectilinear. Hence, the system under consideration does not obey the relation in equations (2) and (3) despite the occurrence of the previously mentioned crossover which is characteristic of spinodal decomposition. Here, $S_m/S_c = 2^{-1}$ which shows that the relation $S_m/S_c = 2^{-\frac{1}{2}}$, peculiar to spinodal decomposition and to block polymers for various temperature, does not apply. For these reasons it is concluded that the system studied in contrast to linear block polymers has definite obstacles to relaxation to a thermodynamically-stable state. As a consequence, the stability of a new-equilibrium state arising during the

temperature change is maintained by elastic stresses. In terms of formal relations such as that in equation (3) it means that the deviation from rectilinear dependence observed in *Figure 5* is due to the temperature dependence of $\alpha(s)$. For a polymer network the latter is expected as a space joint places restraints on the mobility of chemically distinct blocks. It is evident that such a system may maximally approach equilibrium state at temperatures near the temperature of network polymer formation (in present case, 110°C). Cooling below this temperature or heating significantly above it lead to a non-equilibrium state due to stable entanglements of the network polymer chains. It is not until stressed chain rupture that transition from the non-equilibrium to an equilibrium phase state would have proved possible.

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