Macromolecules **1994,** *27,* 2345–2347

Communications to the Editor

Structural Studies of Thermoplastic Triblock Copolymer Gels

N. Mischenko,† K. Reynders,† K. Mortensen,‡
R. Scherrenberg,† F. Fontaine,† R. Graulus,§ and
H. Reynaers*,†

Laboratorium voor Macromoleculaire Structuurchemie,
Departement Scheikunde, Katholieke Universiteit Leuven,
Celestijnenlaan 200F, B3001 Heverlee, Belgium, Physics
Department, Risø National Laboratory, DK-4000 Roskilde,
Denmark, and Raychem N.V., Kessel-Lo, Belgium

Received October 26, 1993
Revised Manuscript Received February 1, 1994

Formulating certain styrenic triblock copolymers with a midblock-selective solvent results in a soft, highly elastic gel with thermoplastic properties.[1,2] The triblock copolymers used in this study are of the type ABA where A represents a glassy polystyrene end block and B represents an elastomeric midblock of the type poly(ethylene–butylene). Several grades are commercially available from Shell under the tradename Kraton G.

Thermoplastic gels were made by mixing Kraton G polymer with a hydrocarbon oil at elevated temperatures. The extender fluid used was a highly refined, aromatic-free, "paraffinic oil" which is a mixture of saturated aliphatic and alicyclic hydrocarbons. These oils have a solubility parameter close to that of the elastomeric midblock and are quasi incompatible with the polystyrene end blocks of the triblock copolymers. Plaques of suitable thickness for small-angle scattering measurements on these gels were made by high-temperature compression molding.

The variety of existing types of ABA block copolymers allows exploration of a broad spectrum of gel formulations as a function of block chemical nature, lengths and ratios. Here we report the results of a first study devoted to Kraton G1651 and Kraton G1650 gels (see Table 1).

The SAXS patterns were recorded using Ni-filtered Cu Kα radiation in conjunction with a Kratky-type (Rigaku) camera (entrance slits 40 or 70 μm) mounted on a Rigaku Rotaflex rotating anode (7.5 kW). The detection device was a Braun one-dimensional position-sensitive counter.[3] Some of the measurements were obtained from an Anton Paar Kratky compact camera. Data treatment was done using the program FFSAXS5.[4]

Preliminary experiments of neutron scattering were made at the cold source of the SANS facility[5] at Risø National Laboratory.

Table 1. Characteristics of the Kraton Gel Polymers

sample	MW[a] total	MW[a] midblock	MW[a] end block	conc PS[b] (wt %)	conc triblock (wt %)
G1651	240 000	160 800	39 600	33	2, 4, ..., 18, 20
G1650	100 000	71 000	14 500	29	7, 8.5, 12

[a] The molecular weights are number-average molecular weights, M_n, measured by GPC (data expressed as polystyrene equivalent molecular weight). [b] The concentration of polystyrene is a weight percentage and is measured by NMR.

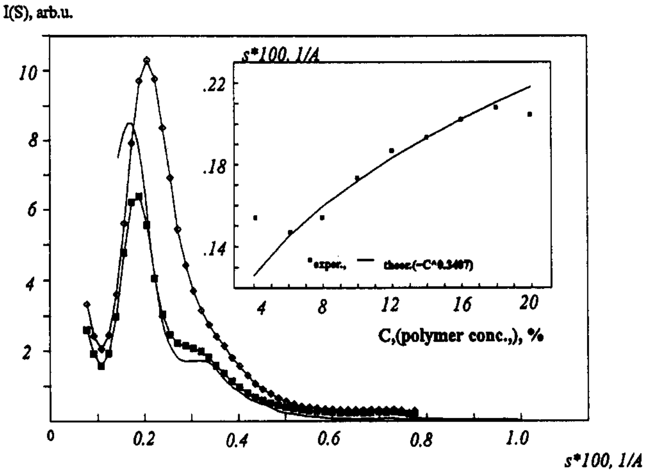

Figure 1. Experimental patterns of SAXS (full curve, 12% of polymer) and SANS (■, 12%; ◇, 20% of polymer) for G1651 gels. Two interference maxima are well pronounced. Their positions shift to larger angles with increasing polymer concentration (the dependence for the first one can be seen in the inset).

Most of the SAXS curves of both types of Kraton gels exhibit two well-pronounced maxima in complete agreement with the results from neutron scattering (SANS). It can be observed from these SAXS and SANS patterns that the position of both maxima shifts to higher s-values with increasing concentration of polymer (Figure 1). The second maximum is always less pronounced and in addition disappears with increasing block copolymer concentration of the gel. Other observations are to be noted for the gel prepared on the basis of Kraton G1651: on a logarithmic scale an additional concentration-independent side maximum (the same one has been detected by Pleštil et al.[6]) appears at a reciprocal distance of about $S = 0.0075$ Å^{-1} ($S = 2(\sin\theta/\lambda)$); another point of interest is the presence of a shoulder on the low-angle side of the first maximum, which is only detected by the Kratky compact camera.

For the G1651 samples, the half-width of the principal peak decreases with increasing concentration up to 12% copolymer concentration and increases again for higher concentration. A similar observation is made for the G1650 samples although in this case the concentration range is restricted between 7% and 12%.

The poly(ethylene–butylene) phase has a low glass transition temperature (T_g), while the polystyrene phase has a T_g near 90 °C. Heating the sample above 90 °C would influence the electron density difference between the two phases. As illustrated in Figure 2, the evolution of the intensity of the main maximum reveals a transition temperature near 90 °C and thus could be an indication of the T_g of polystyrene in the Kraton gel. At the same time, a distinction has to be made for copolymer concentrations below or above 12% in the case of the G1651 samples. Below 12%, the maximum intensity increases beyond the transition temperature but decreases for a copolymer concentration above 12%.

---

† Universiteit Leuven.
‡ Risø National Laboratory.
§ Raychem N.V.

0024-9297/94/2227-2345$04.50/0

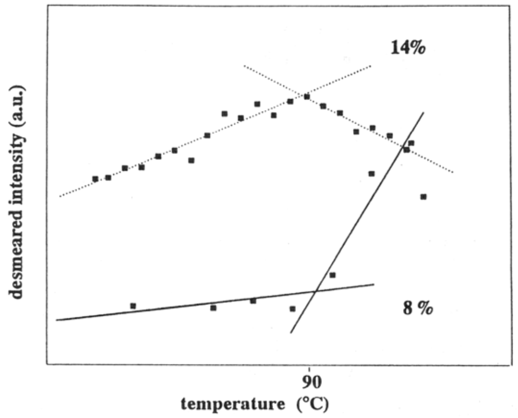

Figure 2. Temperature dependence of the intensity of the first maximum of SAXS curves for the systems with a concentration lower and higher than 12%.

It was not possible to determine the transition temperature of the G1650 samples: they flow at approximately 80 °C.

Deformation of the samples results in a redistribution of the intensity of the originally isotropic two-dimensional SANS patterns. The deformation behavior of 20% Kraton gel is of special interest. For $K < 2.5$ the maximum position along the axis of elongation decreases to $S_{\max}/K$ and in the perpendicular direction increases to $S_{\max}*\sqrt{K}$, where $S_{\max}$ is the original position of the first maximum and K is the elongation. This points to an affine deformation of the three-dimensional network of domains. For extensions of $K = 2.5$ the correlation peak, perpendicular to the elongation, vanishes. However, we observed full reversibility of deformation; hence, these gels are thermodynamically stable systems.

Because the two well-pronounced maxima observed in the scattering patterns shift with increasing concentration, it is concluded that they are due to interdomain interference. This point of view is also supported by the smaller spacings observed for the G1650 samples which have a lower molecular weight, i.e. a shorter chain length, of the rubber midblock and polystyrene end blocks. The side maximum (which is most detectable for 20% G1651 gel) can provide information on the dimensions of the polystyrene domains.

The 12% copolymer concentration appears as a transition concentration. The increasing half-width of the two main peaks for higher concentration of G1651 and the gradual disappearance of the second maximum can be interpreted as an evolution to a less ordered system. However, the opposite dependence of the half-width versus polymer concentration between 2% and 12% suggests that another type of domain arrangement is more suitable at higher concentration; so the system has to change from the former type of order to a new one. Other evidence for this hypothesis is the different temperature dependence of the intensity of the first maximum in the scattering function for the gels with polymer concentration lower and higher than 12%. Finally, a last point to be considered is the affine character of the deformation of the gels. A potential model will now be proposed which accounts for most of the experimental observations.

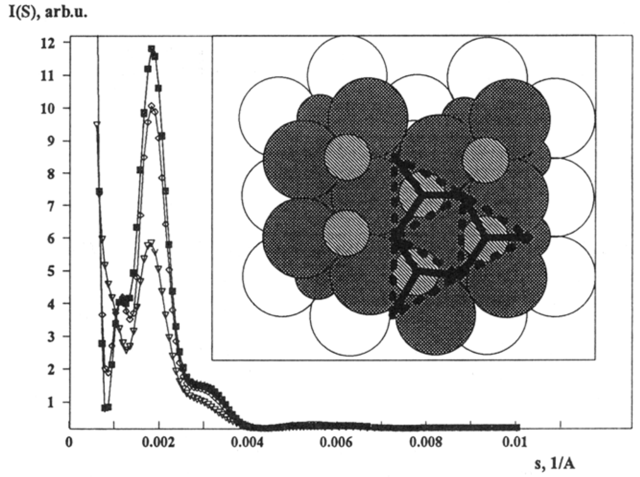

Figure 3. Calculated intensity curves for three-dimensional tetrahedral (■) and two-dimensional hexagonal (▽) models of PS domain arrangement without any effects of disorder (see schematic picture in upper right corner). At the left side of the first maximum of the curve corresponding to the 3D model, a shoulder appears which is detected in the experiments with a Kratky compact camera (◇), for which the most favorable measurement conditions are realized.

There are several approaches to analyze SAXS and SANS patterns, depending on different types of ordering: (1) in the case of crystalline structure we have to find some appropriate type of crystalline lattice; (2) a liquidlike type of ordering, involving only nearest-neighbor distances, can be analyzed by a radial distribution function (RDF); (3) finally, a liquidlike type of order with nonisotropic coordination of nearest neighbors can be supposed, which needs direct calculation of the model intensity.

The scattering patterns are characterized by relatively broad peaks, revealing only short-range order interdomain distance correlation. Although micellar solutions of block copolymer even in crystalline phases can show liquidlike correlation in the intermicellar distances,[5] there is no indication that any of the present samples have a crystalline type of order. (This will be discussed further in a forthcoming paper.[7]) We will therefore in the following assume a liquid type of ordering.

The neutron-scattering pattern can be analyzed analytically in terms of a network of PS micelles, for example, with effectively hard-sphere interaction potential (the RDF route discussed above). This gives high-quality fits with surprisingly good correspondence between the known amount of polystyrene and the value obtained from the fits assuming that the PS domains are equal to the micellar cores. The hard-sphere analysis for all samples resulted in hard-sphere volume fractions which are below 0.45, i.e., below the critical value for crystal formation,[5] thus supporting the liquidlike structure. Analysis in terms of hard-sphere interaction will be further elaborated.[7]

An alternative approach to analyze the data is in terms of fitting to a direct model, taking into account the distances and coordination between nearest neighbors.

A variety of coordination types of neighboring PS domains around a central PS domain can be considered and checked. A more straightforward way is to model the process of gel formation. The concentration of (PE/PB + solvent) is much higher than the concentration of PS. We assume that the gelation process involves a phase-separation step resulting in the formation of large regions filled with the solvent, containing the hydrogenated polybutadiene midblock (large particles). The process of microphase separation leads also to the formation of smaller domains of insoluble PS blocks in spaces between close-packed large particles. Analysis of the three-dimensional arrangement of spaces between close-packed spheres results in two different kinds of cavities, one with their centers positioned on the boundary region between two layers of large particles and the other with the center of the cavities within a plane of large particles. The filling of the former ones is more favorable for the obtention of a minimum surface energy, at least at low concentrations. Three potential situations now emerge. Two of them deal with a tetrahedral coordination of the nearest-neighbor domains (see the inset in Figure 3), and the third one refers to a hexagonal arrangement of PS domains. A full description of the model considerations will be presented in a subsequent paper.[7] The last (hexagonal) arrangement gives the possibility of short cylindrical PS domain formation which can be the intermediate elements of bulk Kraton G1651 morphology.

Short-range ordering of PS domains, connected into a three-dimensional network, allows us to use the Debye formula:[8,9]

$$I(S) = F_{\mathrm{sph}}{}^2(2\pi S)\left[N + 2\sum_{i\neq j} Z_{ij}\frac{\sin 2\pi SR_{ij}}{2\pi SR_{ij}}\right]$$

where Z_{ij} takes into account the disordering factor, to simulate the experimental intensity data of the gels (Figure 3). The calculation reproduces correctly the position of both principal maxima as well as the intensity ratio of these peaks. If we suggest that a change of the disordering factor of PS domain arrangement occurs with an increase of concentration or temperature, then we are able to explain as well the changes in width and height of the maxima as a function of temperature and polymer concentration.

A similar idea has been used previously by one of us.[10]

Acknowledgment. This research program was financially supported by the Flemish Institute for the promotion of Scientific–Technological Research in Industry (I.W.T.) for which we are very grateful. H.R. is indebted to the FKFO of Belgium for scientific support.

References and Notes

(1) Patents EP-A-029978, U.S. 5149736 and WO-A-9305113.
(2) Shell Technical Bulletins SC 1102-89 and SC 198-92.
(3) Defoor, F.; Groeninckx, G.; Reynaers, H.; Schouterden, P.; Van der Heijden, B. *Macromolecules* **1993**, *26*, 2575.
(4) Vonk, C. G. *J. Appl. Crystallogr.* **1971**, *4*, 340.
(5) Mortensen, K.; Brown, W.; Nordén, B. *Phys. Rev. Lett.* **1992**, *68*, 2340.
(6) Pleštil, J.; Hlavatá, D.; Hrouz, J.; Tuzar, Z. *Polymer* **1990**, *31*, 2112.
(7) Mischenko, N.; Reynders, K.; Mortensen, K.; Fontaine, F.; Reynaers, H., to be published.
(8) Kratky, O. In *Small-Angle X-ray Scattering*; Glatter, O., Kratky, O., Eds.; Academic Press: London, 1982.
(9) Mischenko, N.; Reynders, K.; Fontaine, F.; Reynaers, H. *Abst. IXth Int. Conf. SAS* (*Saclay, Fr.*) **1993**, P10.
(10) Mischenko, N. *Abst. XVth Congr. Union Crystallogr.* (*Bordeaux, Fr.*) **1990**, C195.