Physical Gelation of a Multiblock Copolymer: Effect of Solvent Type

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ABSTRACT: The physical gelation of an organosilicic multiblock copolymer (poly(dimethylsiloxane)–poly[1-(dimethylsilyl)-4-[(dimethylvinyl)silyl]benzene]) has been studied with regard to the solvent type. It is shown that the temperature–concentration phase diagrams are similar. This particularly means that the gelation mechanism proceeds via liquid–liquid phase separation frozen in at its early stage by crystallization whatever the solvent used. The compression modulus E is determined as a function of temperature and concentration C. In the latter case it is found that, independent of the solvent, E varies as

$$E \sim X^2C^{4.6\pm0.3}$$

in which X is the crystalline block weight fraction of the copolymer. A short theoretical derivation is given which provides the following expression:

$$E \sim X^2C^5$$

Finally the morphology and the swelling behavior are examined. The main conclusion of this study is that the solvent type has very little influence on the gel properties as opposed to what is found with other polymers such as isotactic polystyrene or isotactic poly(4-methylpentene-1).

Introduction

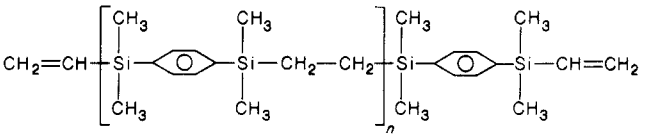
The phenomenon of thermoreversible gelation embodies a large number of differing systems, from biological macromolecules to synthetic polymers. Whereas the former have been and still are widely studied,[11] the latter lack experimental knowledge in spite of a growing number of publications in the domain.[2-16]

Among the synthetic polymers capable of forming physical gels, multiblock copolymers are of special interest. Their chain architecture and, particularly, the proportion of crystallizable blocks to the amorphous ones can often be controlled at will. Thanks to this versatility, these copolymers can be, to some extent, used as model chains of homopolymers containing long enough stereoregular sequences. In this respect, recent results gained on a silicic copolymer of low crystalline block content[17,18] proved to be useful to provide the findings of Mutin et al. on PVC gels[19] with additional support. Indeed, the hundredfold discrepancy which exists between modulii of PVC gels and of 10% crystalline copolymers corroborates the existence, in the former, of physical links other than those arising from the crystallization of syndiotactic sequences.

Hitherto, we have only investigated the physical gelation of solutions of this copolymer in *trans*-decalin. In this paper, we report on a new study dealing with the effects of the solvent type. This work is motivated by the frequently accepted idea, based on various experimental results,[5,12,14] which considers that the solvent participates in the formation of physical junctions in some systems. The feasibility of polymer–solvent compounds with apolar solvents has been recently demonstrated in the system PEO–parahalogeno disubstituted benzene.[20] The compound is even more stable than the pure polymer crystals. Clearly, the solvent type influence must be investigated to discover whether the same situation is encountered here.

Experimental Section

Materials. In this study a multiblock copolymer has been used which is composed of flexible poly(dimethylsiloxane) blocks (PDMS) and crystallizable poly[1-(dimethylsilyl)-4-[(dimethylethylene)silyl]benzene] blocks (COSP = crystalline organosilicic polymer):



This synthesis of this block copolymer was carried out following the method devised by Prud'homme.[21] Further details about the preparation procedure are available in ref 17 and 18.

Three samples with different contents of crystalline component (X_{COSP} in w/w) were used. These samples, designated as Copo10, Copo20, and Copo50 possess the characteristics detailed in Table I.

Three solvents of high-purity grade were employed without further purification. These are *trans*-decalin, bromobenzene, and 1-phenyldodecane.

Sample Preparation. Gels were produced from homogeneous solutions prepared at 175 °C in *trans*-decalin and 1-phenyldodecane and 150 °C in bromobenzene (in the latter case higher temperatures could be used for more concentrated solutions). These solutions were then quenched at −18 °C (*trans*-decalin and bromobenzene gels) or at 20 °C (1-phenyldodecane gels) for 24 h so as to complete gelation. As in previous works,[17,18] the gels were kept for a week at 30 °C prior to any measurements.

In order to understand the copolymer crystallization behavior, the knowledge of the phase diagrams of the crystalline block in the same solvents is necessary. These diagrams were established with samples prepared under the same conditions as the gel samples.

Techniques. Thermal Analysis. DSC II and DSC 4 from Perkin-Elmer were used. Data were processed by means of the TADS system (thermal analysis data station). Experiments were performed at different heating rates; yet the standard 20 °C/m heating rate was employed to establish the phase diagrams. Calibrations were obtained from an indium standard. To achieve solvent crystallization in the gel samples, low cooling rates ranging from −2.5 to −1 °C/min were used.

Approximately 10 mg of freshly prepared sample were placed into a "volatile sample" pan which was then tightly sealed. The gel–pan contact was improved by remelting the sample at 175 °C (or 150 °C with bromobenzene) then quenching again at the subsequent temperature for 24 h. As said above, the samples were stored at 30 °C for a week. While this last step does not markedly alter the overall thermal behavior, it enables one to notably

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Table I
Characteristics of the Different Samples[a]

sample	$M_{nCOSP}(1)$	M_{nPOMS}	X_{COSP}	$M_{wCopo}(2)$	$M_{wCopo}(3)$	$M_{nCopo}(3)$	M_w/M_n
Copo10	2000	17000	0.11	215000	192000	88000	2.18
Copo20	4000	17000	0.19	130000	111000	62000	1.79
Copo50	9700	9700	0.5	290000			

[a] 1 = theoretical; 2 = light scattering; 3 = GPC.[17,18]

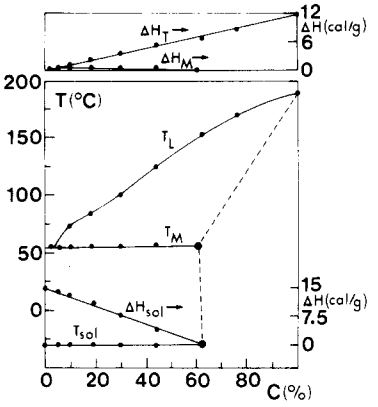

Figure 1. Temperature–concentration phase diagram of COSP (M_w = 9700) in bromobenzene (concentration in w/w).

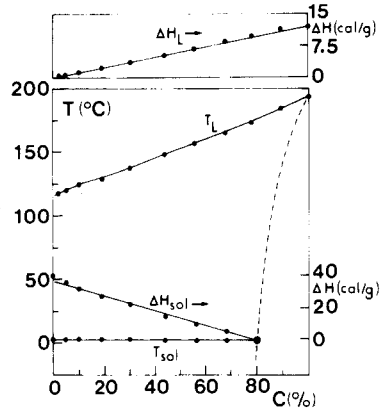

Figure 2. Temperature–concentration phase diagram of COSP (M_w = 9700) in 1-phenyldodecane (concentration in w/w).

improve the quality and resolution of the DSC thermograms.

Turbidimetry. The determination of the coexistence curves was achieved by means of a turbidimeter devised by F. Debeauvais from our laboratory. Cooling rates ranging between 0.1 and 1 °C/min were used.

Mechanical Properties. A mold with parallel surfaces was used in order to produce gel slabs of 1-cm thickness. These slabs were thermally treated as described above. Afterward, cylinders of 1.5-cm diameter were cut off to perform mechanical testing.

Compression moduli determination was carried out with an apparatus described elsewhere. The gels were kept immersed in water, whose temperature was thermostatically monitored by an outer water circulation. Decalin and, to a lower extent, bromobenzene and 1-phenyldodecane are incompatible with water which results in no significant alteration of the piece of gel and, correspondingly, no detectable effects on the modulus.

As usual, the compression modulus E was determined from the relation

$$\sigma_R = E(\lambda - 1/\lambda^2) \quad (1)$$

where σ_R is the reduced stress and λ the strain. $\lambda = l/l_0$, l_0 being the sample's initial height.

Morphology. Gel morphology was investigated by optical microscopy using a Zeiss photomicroscope II.

Results and Discussion

Thermal Behavior. Phase Diagrams. COSP–Solvent Systems. It was shown in previous publications[17,18] that the couple COSP–*trans*-decalin possesses a miscibility gap. The effects of this miscibility gap manifest themselves only when a rapid quench to low temperatures is brought about. It is revealed quite simply in the temperature–concentration phase diagram by a monotectic transition located near 50 °C and by a crystal morphology that differs whether crystallization occurred prior to or after liquid–liquid phase separation.

The same phenomenon occurs in the COSP–bromobenzene system as shown in Figure 1 in which the temperature–concentration phase diagram is drawn. This diagram is quite similar to the COSP–*trans*-decalin system's. Particularly, it also displays a monotectic transition in the vicinity of 50 °C.

The results gained on the COSP–1-phenyldodecane are somewhat at variance with those given above. As can be seen in Figure 2, in which the temperature–concentration phase diagram for samples quenched at 20 °C is given, no monotectic transition is observed. This absence seems to some extent paradoxical in the light of the results obtained with *trans*-decalin and bromobenzene. As a matter of fact, the liquidus line varies only slowly as a function of concentration in 1-phenyldodecane whereas the decrease is steeper in *trans*-decalin and bromobenzene. Flory's relation allows,[22] in a first approximation, calculation of this line through the knowledge of the polymer–solvent interaction χ^1:

$$1/T_m - 1/T_{mo} = (v_1 - \chi_1 v_1^2)RV_u/\Delta H_u V_1 \quad (2)$$

where T_m and T_{mo} are the melting temperatures of the pure polymer and of the polymer in presence of solvent, respectively, v_1 is the volume fraction of solvent, R is the gas constant, V_u and ΔH_u are the molar volume and the heat of fusion per repeating unit, and V_1 is the molar volume of the solvent.

This relation entails that the better the solvent, the steeper the decrease of the liquidus line with decreasing polymer concentration. Accordingly, 1-phenyldodecane is by far a poorer solvent than *trans*-decalin or bromobenzene and one would expect to also observe the effect of a miscibility gap.

A clue to this apparently paradoxical situation lies in a series of annealing experiments carried out at high tem-

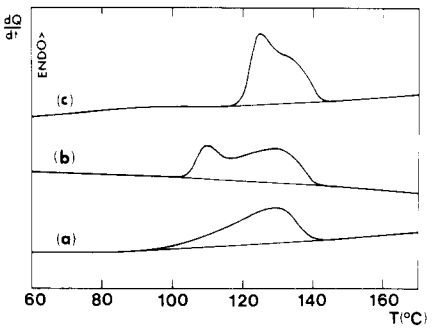

Figure 3. DSC thermograms (20 °C/min) of a 10.4% COSP–1-phenyldodecane solution: (a) crystallized by a quench at 20 °C; (b) after annealing (a) for 12 h at 85 °C; (c) annealing (a) for 12 h at 100 °C.

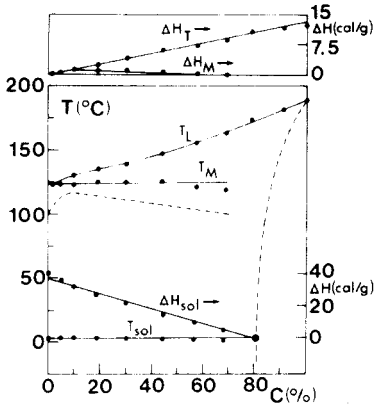

Figure 4. Temperature–concentration phase diagram obtained after annealing at 100 °C COSP-1-phenyldodecane solutions quenched at 20 °C (concentration in w/w).

peratures. For samples crystallized through a rapid quench at 20 °C and then annealed at 85 °C or above, the following results are obtained (see Figure 3): (i) After annealing, the melting endotherm is composed of two peaks. (ii) The maximum of the low melting temperature peak is invariant with polymer concentration (see Figure 4). (iii) The total melting enthalpy (low + high melting peaks) has increased by approximately 20%. This gives, after annealing, a degree of crystallinity close to 100% if one uses $\Delta H = 13.6$ cal/g for the totally crystallized COSP. (iv) The melting enthalpy of the low melting temperature peak increases at the expense of the high melting temperature endotherm.

The following explanations can account for these results. When the sample is rapidly quenched at 20 °C, only 80% of the polymer has crystallized, the crystals being far from perfect under these conditions. As usual, annealing allows crystallization to be completed or/and crystals perfection to be improved (thickening process for instance). At 85 °C and above, part of the crystallized material undergoes melting which involves the most imperfect crystals. This apparently helps trigger the crystallization of the remaining amorphous material. We attribute the invariance of the low melting temperature peak with polymer concentration to the annealing process taking place within a miscibility gap. Once molten the polymer in solution first undergoes liquid–liquid phase separation which creates a polymer-rich phase of always the same composition in spite of a varying initial polymer concentration. As a result, crystals grown from this phase will always have the same melting point. From this argument we show that there does exist a miscibility gap which lies well below the crystallization line. In Figure 4 is drawn a possible location for the miscibility gap as deduced from the annealing experiments. This gap is certainly unattainable at the cooling rate used without alteration of the solution. According to a thermodynamic argument developed by Cahn,[23] if the crystallization is at its later stage, the crossing of the coexistence curve should not alter the process. This argument gives an acceptable explanation of why the monotectic transition was not observed in the first place despite the poor solvent quality of 1-phenyldodecane.

PDMS–Solvent Systems. As already mentioned, *trans*-decalin is a good solvent for PDMS. Bromobenzene is reported to be a Θ-solvent for $T = 78.5 \pm 2$ °C.[24] Similarly, 1-phenyldodecane happens to be a very poor solvent at room temperature as well. From turbidimetry experiments the determination of the coexistence curves has been achieved. The temperature–concentration phase diagrams are drawn in Figure 5 for $M_{wPDMS} = 1.7 \times 10^4$. It is found that $T_c = 85.2 \pm 0.5$ °C in 1-phenyldodecane and $T_c = 40.8 \pm 0.5$ °C in bromobenzene.

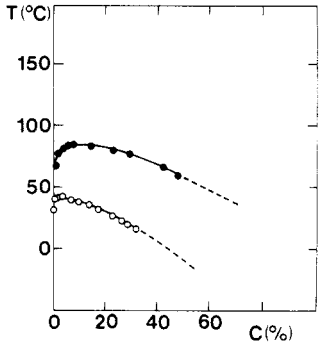

Figure 5. Temperature–concentration phase diagrams for PDMS ($M_w = 17\,000$) in bromobenzene (○) and 1-phenyldodecane (●) showing the coexistence curves (concentration in w/w).

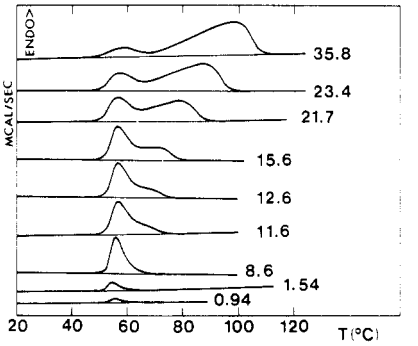

Figure 6. DSC thermograms for Copo50 in bromobenzene after quenching to −18 °C for 24 h and then annealing 7 days at 30 °C. Heating rate 20 °C/min. Concentrations in percent (w/w) as indicated.

These results together with those obtained in the COSP lead to the conclusion that in 1-phenyldodecane and in bromobenzene the PDMS–COSP multiblock copolymer ought to inevitably exhibit a miscibility gap above room temperature.

Gel Samples. In previous papers,[17,18] we showed that gel formation mechanism in *trans*-decalin at low quenching temperatures proceeds from liquid–liquid phase separation frozen in at its early stage by crystallization. Worth underlining is that such a mechanism is quite common in physical gelation.[25,26] For this mechanism to occur, it is compulsory that the system be quenched, unaltered, within a miscibility gap. This mechanism turns out to also occur in the Copo10–*trans*-decalin system which suggests that the COSP block strongly governs copolymer–*trans*-decalin interactions. As stressed above, the situation is quite different with bromobenzene and 1-phenyldodecane in the sense that, whatever the composition, these systems will certainly possess a miscibility gap at room temperature.

In Figure 6 are drawn typical DSC thermograms for different polymer concentrations in bromobenzene. Similar thermograms are obtained with 1-phenyldodecane gels.

As with *trans*-decalin gels, below a concentration C_M, there is only one endotherm, the position of which does not vary with concentration. For concentrations larger than C_M, a second endotherm appears at higher temperature. For a concentration C_α the low melting endotherm eventually vanishes.

The phase diagrams determined from the thermal behavior are drawn in Figure 7 for bromobenzene and Figure 8 for 1-phenyldodecane. As can be seen, they are similar to those established in *trans*-decalin gels. However, while the different transitions in bromobenzene do not markedly differ from those in *trans*-decalin, the monotectic transition and the liquidus line are shifted to higher temperature in 1-phenyl dodecane gels. This result is expected in the

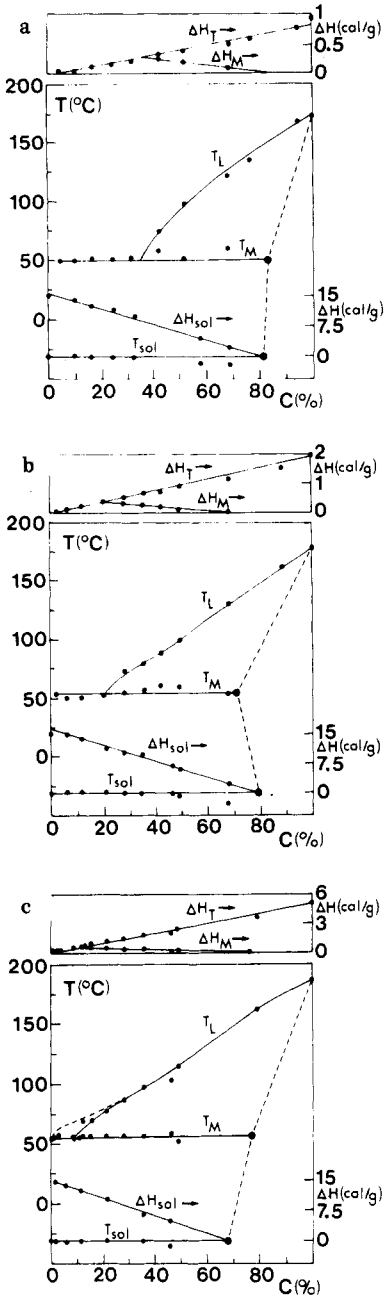

Figure 7. Temperature–concentration phase diagrams for copolymer–bromobenzene gels quenched at −18 °C for 24 h and then annealed 7 days at 30 °C: (a) Copo10; (b) Copo20; (c) Copo50. (Concentration in w/w.)

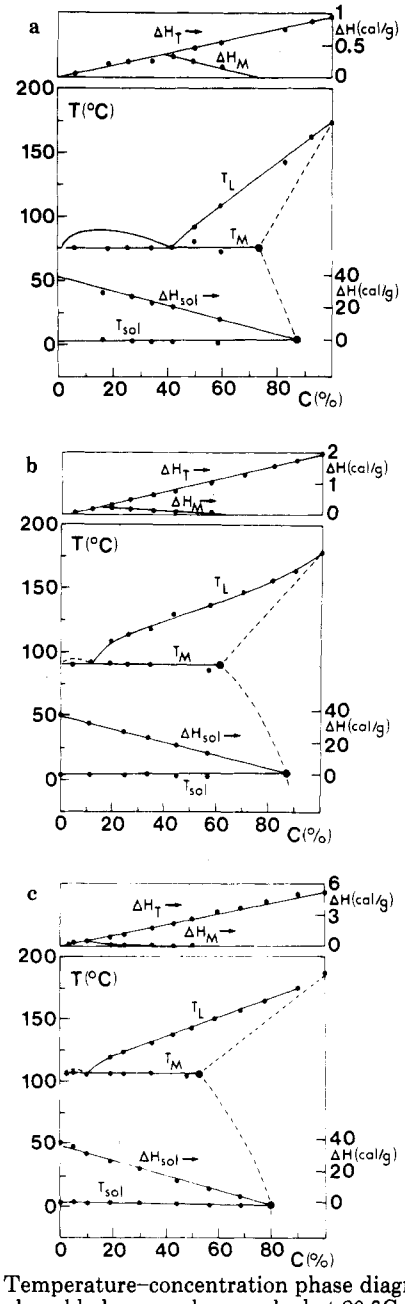

Figure 8. Temperature–concentration phase diagrams for copolymer–1-phenyldodecane gels quenched at 20 °C for 24 h and then annealed 7 days at 30 °C: (a) Copo10; (b) Copo20; (c) Copo50. (Concentration in w/w.)

light of the data obtained on the COSP–1-phenyldodecane mixtures. Equation 2 implies that the liquidus line be located at higher temperatures, a condition which also holds for the monotectic transition.

Unlike *trans*-decalin and bromobenzene, the coexistence curve in the Copo10–1-phenyldodecane system is unambiguously observed above the monotectic transition. With Copo20 and Copo50 there is a doubt as to whether the coexistence curve is really seen above the monotectic line, hence the use of a dashed line.

As was already noticed and discussed in the case of Copo–*trans*-decalin gels, the monotectic concentration C_M decreases with increasing the crystalline block content X_{COSP}. We have attributed this effect to the relation that ought to exist between the concentration reached by the polymer-rich phase just before crystallization takes place and the monotectic concentration C_M. It is even suspected that both concentrations are equal. It then seems legitimate to infer that the faster the crystallization kinetics, that is the higher the COSP content, the lower this concentration.

Finally, there is no indication as to the formation of a polymer–solvent compound. The total melting enthalpy (high + low melting endotherms) extrapolates for $C = 1$ to a value close to that of the pure COSP block,[27] which suggests that an identical crystalline lattice is involved. This point was further tested by X-ray diffraction on Copo50–*trans*-decalin gels (see ref 18).

Morphology. Investigation of physical gel morphology is not a straightforward task. The use of electron microscopy involves a special sample treatment which usually involves a drying process. To what extent the original gel structure is affected is difficult to say. While the use of optical microscopy avoids tampering with the sample, the resolution is generally too low. However, in the present case, the structures are large enough to be evidenced by the latter technique.

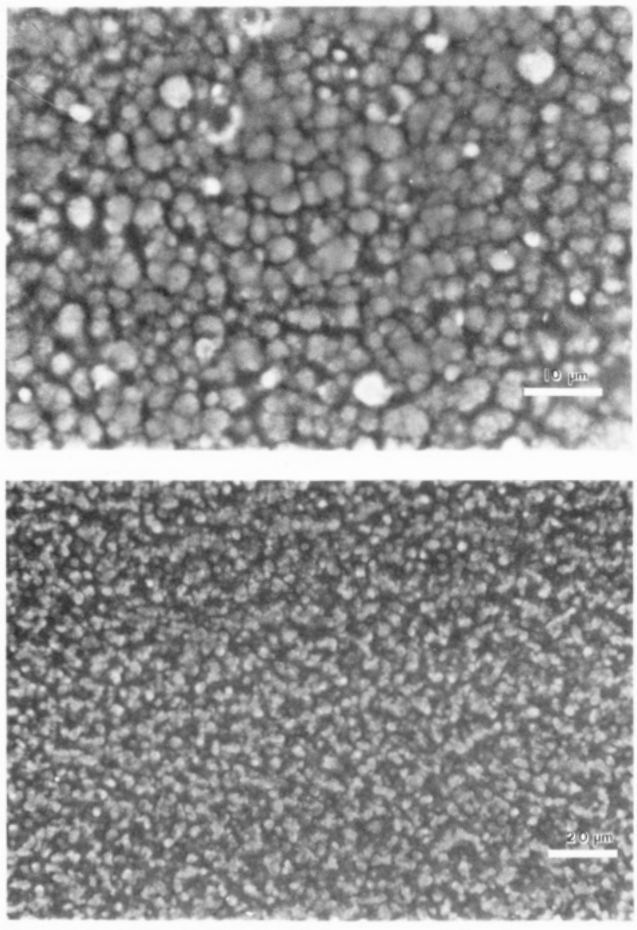

Figure 9. Optical micrographs by means of the phase contrast method of (a, top) Copo20 10% in 1-phenyldodecane and (b, bottom) Copo50 10% in bromobenzene prepared as above.

In Figure 9 are given optical microscope pictures of gels in bromobenzene and 1-phenyldodecane. As expected, the structure is networklike (it could have been spherolitic). On an average the mesh size lies somewhere between 0.5 and 5 μm. This type of structure is reminiscent of what has been found with gels of other polymers.[8,26] These observations provide support for the theoretical model put forward to account for the swelling behavior of Copo–*trans*-decalin gels (see ref 17 and 18). It must be stressed that concerning the latter, only a salt-and-pepper structure can be seen. We accordingly infer that only the scale is different (shorter mesh in *trans*-decalin gels). We do not know currently the exact origin of a shorter mesh. This may stem from the fact that decalin is a good solvent for the PDMS block. As a result, the amorphous region will swell far more in *trans*-decalin than in the other solvents. This may hamper the lateral growth of the fiber due to density constraints at the amorphous–crystal interface, a phenomenon pointed out by Guttman et al. from theoretical arguments.[28] As a speculation, we suppose that this effect may produce smaller structures.

Finally, it is worth noticing that these structures resemble closely those expected when the liquid–liquid phase separation proceeds via spinodal decomposition.[25,29] This mechanism is frequently considered as probably being involved in most of the physical gel formation process.

Mechanical Testing. As usual, stress relaxation and the compression modulus have been investigated, the latter as a function of both temperature and polymer concentration.

Stress Relaxation. For all the gels studied here, the stress relaxation at constant deformation reads

$$\sigma \sim t^{-m} \tag{3}$$

The value of m is somewhere between 0.015 and 0.03. There is no particular correlation of this parameter with the solvent type. The values are typical of what is measured for chemically cross-linked gels whose cross-links are fixed.[30] Similar values are found with PVC gels for which evidence supports the existence of crystalline gel junctions.

As already emphasized elsewhere, these values contrast with those reported for iPS gels[31] ($m \simeq 0.1$–0.15, depending on the solvent). On the basis of recently reported neutron diffraction experiments[32] intended to investigate the molecular structure, it has been concluded that the iPS structure is liquid crystalline like rather than crystalline. Accordingly, the physical links are supposed to be more mobile, a statement in agreement with the high mobility revealed by stress relaxation experiments.

The results reported here might eventually imply that relaxation behavior similar to that of a chemical gel is a hint of true crystalline links. The parameter m could be used as a straightforward criterion to differentiate crystalline from noncrystalline gels.

Compression Modulus as a Function of Temperature. In order to account for the variation of the compression modulus as a function of temperature in Copo–*trans*-decalin gels, we developed a phenomenological theory based on the concept of partial melting.[17] It is stated that the gel melts partly at T_M for $C > C_M$. This approach is at variance with a common idea that assigns the low melting endotherm to the gel melting and the high melting endotherm to the fusion of chain-folded crystals.[2] While the latter rationale holds for some physical gels such as iPS gels, it does not pertain to the gels studied here.

In the partial melting approach the compression modulus is taken as being proportional to the content of the polymer-rich phase. Considering the ratio of the modulus at temperature T, $E(T)$, to the modulus at 20 °C, $E(20)$, one ends up with the following relations:

for $C < C_M$

$$E(T)/E(20) = 1 \quad \text{for} \quad T < T_M$$
$$E(T)/E(20) = 0 \quad \text{for} \quad T \geq T_M$$

for $C \geq C_M$

$$E(T)/E(20) = 1 \quad \text{for} \quad T < T_M$$
$$E(T)/E(20) = [(C_{prep} - C_{M1}(T)/(C_{\alpha s}(T) - C_{M1}(T))]C_\alpha/C_{prep} \quad \text{for} \quad T \geq T_M \tag{4}$$

where C_{prep} is the polymer concentration, C_α is the solid solution composition at $T = T_M$, and $C_{M1}(T)$ and $C_{\alpha S}(T)$ are the variations of the liquidus line and of the solidus line for $T \geq T_M$, respectively.

As already detailed in the experimental section, the modulus measurements as a function of temperature were carried out in water. This resulted in limiting the temperature range from 20 to 70 °C.

In parts a and b of Figures 10 is drawn the compression modulus behavior in 1-phenyldodecane for Copo20 and Copo50, respectively.

From the approach developed above and considering the phase diagrams in this solvent, a constant value should be obtained in this temperature range. As can be seen, the departure from constancy has a maximum of 20% or so. Taking into account an experimental uncertainty of ±10%, these results are in agreement with the theoretical approach to a first approximation. Discrepancies from this approach may originate in several effects: The effect due to the amorphous sequence is not taken into account. Over a domain of 50 °C the solvent may become better for this

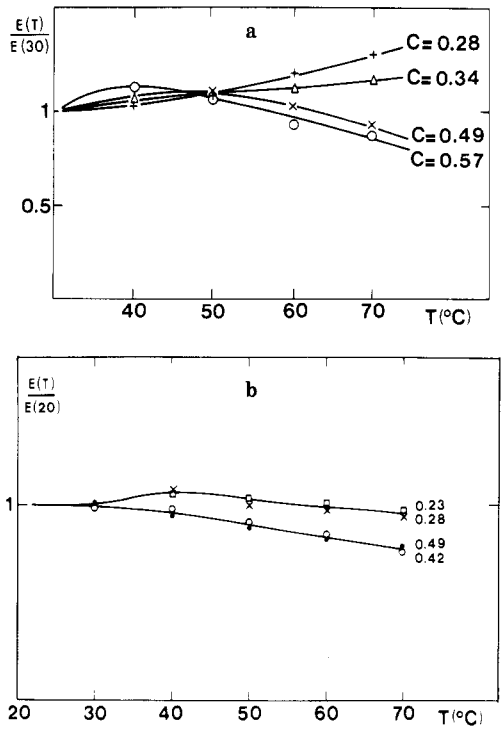

Figure 10. Relative variation of the compression modulus E as a function of temperature T in 1-phenyldodecane: (a) $E(T)/E(30)$ for Copo20 and (b) $E(T)/E(20)$ for Copo50.

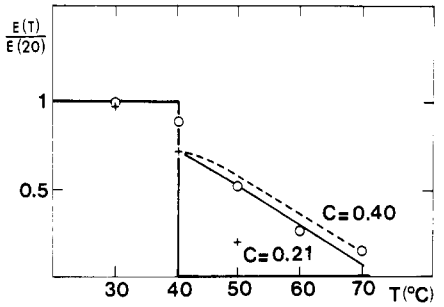

Figure 11. Relative variation of the compression modulus E as a function of temperature, T, $E(T)/E(20)$ for Copo20 in bromobenzene. The full line stands for a solidus line varying as $aT + b$ and the dashed line for a solidus line constant with temperature.

sequence resulting in a change of chain conformation of the PDMS blocks. The fact that the concentrated phase concentration varies quite markedly (probably due to a small swelling of the amorphous sequences) is support of this statement.

As for the gels in bromobenzene, for which a monotectic line exists at 50 °C or so, the partial melting approach allows one to account for the results to a good approximation (see Figure 11).

Compression Modulus versus Concentration and Copolymer Composition. As was reported in previous publications,[17,18] the modulus as a function of polymer concentration C and the weight fraction of crystalline blocks X obeys the following experimental relation (see Figures 12 and 13):

$$E \sim X^2C^{4.6\pm0.3} \tag{5}$$

The only difference between bromobenzene and 1-phenyldodecane on the one hand and *trans*-decalin on the other hand lies in the prefactor which is larger in the latter solvent (see Figure 12). Otherwise, the behavior is quite solvent independent within experimental uncertainties.

The following theoretical analysis is an attempt to account for this behavior. It differs from that previously

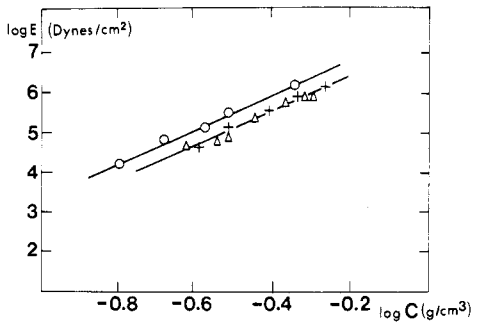

Figure 12. Variation of the compression modulus E as a function of polymer concentration C (in g/cm^3) for Copo20 in (○) *trans*-decalin, (+) 1-phenyldodecane, and (△) bromobenzene.

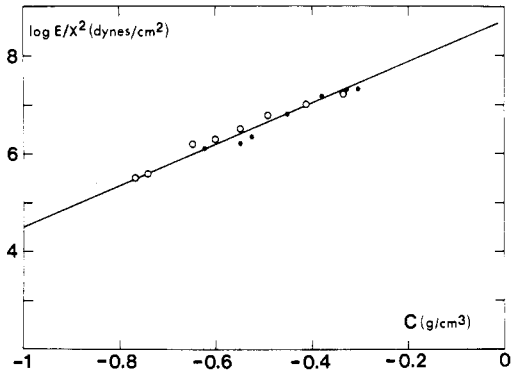

Figure 13. Variation of the reduced modulus E/X^2 as a function of concentration (g/cm^3) for gels from 1-phenyldodecane: (○) Copo50; (●) Copo10.

advanced,[18] yet this new one rests on a firmer theoretical basis.

We shall suppose that the modulus behavior is identical with the osmotic pressure developed by an equivalent solution,[33]

$$E \sim \pi \tag{6}$$

It is known that the osmotic compressibility χ reads

$$\partial\pi/\partial C = \chi^{-1} \tag{7}$$

χ can be calculated from the Fourier transform $S(q)$ of the monomer–monomer correlation function given by the solution in the limit $q \to 0$

$$\lim_{q\to0} S(q) = kTC\chi \tag{8}$$

where k is the Boltzmann's constant, T the temperature, and C the concentration in g/cm^3.

Relations 7 and 8 lead eventually to

$$\partial\pi/\partial C = C \lim_{q\to0} S^{-1}(q) \tag{9}$$

Furthermore, $\partial\pi/\partial C$ can be written

$$\partial\pi/\partial C = \partial C/\partial C_{cry}\partial C_{cry}/\partial C \tag{10}$$

where C_{cry} is the concentration of crystalline species and reads

$$C_{cry} = XC \tag{11}$$

Assuming that the partial osmotic compressibility $\partial\pi/\partial C_{cry}$ reads

$$\partial\pi/\partial C_{cry} = C_{cry}/\lim_{q\to0} S_{cry}(q) \tag{12}$$

we finally end up with

$$\partial\pi/\partial C = X^2C/\lim_{q\to0} S_{cry}(q) \tag{13}$$

$S_{cry}(q)$ is the Fourier transform of the crystal monomer–monomer correlation function $\gamma(r)$ and is given by

$$S_{cry}(q) = \int \langle \delta(0)\delta(\mathbf{r}) \rangle \exp(i\mathbf{qr})\, d\mathbf{r} \qquad (14)$$

where the bracketed expression is the correlation function $\gamma(r)$.

To calculate $S_{cry}(q)$ we shall assume the physical junctions to be crystalline which entails sharp variations in polymer density throughout the sample. Accordingly, the correlation function $\gamma(r)$ can be expressed through the Debye–Bueche's theory[34] derived for inhomogeneous two-density systems with random, spherical orientations:

$$\gamma(r) = \langle \delta(0)\delta(r) \rangle = \exp(-r/a) \qquad (15)$$

Here a represents the distance between inhomogeneities. The calculation of $S_{cry}(q)$ performed by Debye and Bueche[34] gives

$$S_{cry}(q) \sim a^3/(1 + a^2q^2)^2 \qquad (16)$$

In the limit of $q \to 0$ this finally yields for $\partial\pi/\partial C$

$$\partial\pi/\partial C \sim X^2Ca^{-3} \qquad (17)$$

and finally

$$E \sim \pi \sim X^2C^2a^{-3} \qquad (18)$$

We note the symmetry between the crystalline weight fraction and the concentration, a property that was previously suspected.[18] The variation with concentration of the additional term, α^{-3}, is, not experimentally known for the gels under study. However, light scattering experiments carried out on atactic polystyrene pregels[35] have given

$$a \sim C^{-1\pm0.05} \qquad (19)$$

Assuming a similar behavior, we end up with

$$E \sim X^2C^{5\pm0.15} \qquad (20)$$

This theoretical result is in good agreement with the experimental ones. Note that we suppose a to be independant of X. Since the length of a PDMS–COSP sequence does not notably change with varying X, we conclude that, to a first approximation, the distance between crystalline junctions will be independant of X too.

Swelling Behavior. A way of expressing the swelling behavior G_∞ of a gel immersed in an excess of solvent preparation is

$$G_\infty = P_\infty/P_0 \qquad (21)$$

in which P_0 and P_∞ are the initial sample's weight and the sample's weight after swelling to equilibrium, respectively. Considering the gel to be formed of fiberlike structures,[17,18] we have derived an expression for G_∞

$$G_\infty = 1 + (C_\alpha/C_\gamma - 1)X_\alpha \qquad (22)$$

in which C_α and X_α are the concentration and the proportion of solid solution prior to swelling and C_γ the concentration reached by the polymer-rich phase after swelling to equilibrium. To a first approximation X_α reads[17]

$$X_\alpha = C_{prep}/C_\alpha \qquad (23)$$

where C_{prep} is the preparation concentration. If we consider the equilibrium concentration C_{equ}, we have

$$C_{equ} = G_\infty^{-1}C_{prep} \qquad (24)$$

Deviation from the line $C_{equ} = C_{prep}$ in a C_{equ} versus C_{prep} representation indicate swelling if the experimental data are below and deswelling if above.

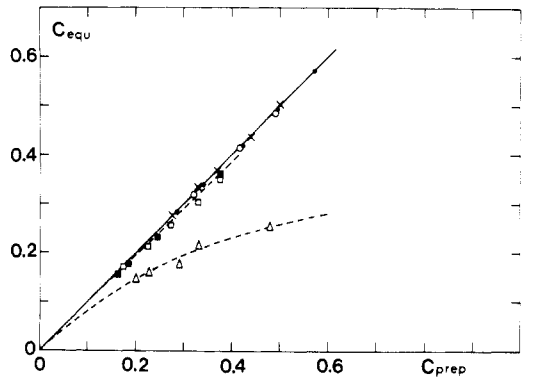

Figure 14. Swelling experiments. Representation of the equilibrium concentration C_{equ} versus the preparation concentration C_{prep}: (△) Copo20 in *trans*-decalin (dashed line calculated from 22 with $C_\gamma = 0.27$); (□ and ■) Copo20 and Copo50, respectively, in bromobenzene (dashed line calculated for Copo20 with $C_\gamma = 0.7$); (○, ●, and ×) Copo10, Copo20, and Copo50, respectively, in 1-phenyldodecane.

As can be seen in Figure 14, and as we already reported,[17,18] *trans*-decalin gels swell in an excess of solvent. The swelling is well-represented by eq 22 by using $C_\gamma = 0.27$.

There is only a very slight swelling in bromobenzene ($C_\alpha = 0.73$ while $C_\gamma = 0.7$ from relation 22). No noticeable swelling can be seen in 1-phenyldodecane. To some extent, as far as swelling properties are concerned, the latter gels can be regarded as being at equilibrium.

Conclusion

In this paper we have evaluated the effect of the solvent type on the physical gelation of a multiblock copolymer. Although the solvents were quite different both in molecular size and in their properties toward the PDMS blocks, we have not been able to point out significantly distinct types of behavior. The gelation mechanism always involves a liquid–liquid phase separation frozen in at its early stage by crystallization, making the phase diagrams look the same. The compression modulus, apart from a difference in the prefactors, exhibits the same scaling law behavior. From the melting enthalpies and from X-ray diffraction experiments,[18] it is concluded that the physical junctions are constituted of crystals possessing the same crystalline lattice as that of the bulk-crystallized state of the COSP block. Clearly, here, unlike with other polymers such as isotactic polystyrene[14,31,32] or poly 4-methylpentene-1,[5] the gelation is scarcely sensitive to the solvent type. This is probably so because the crystalline sequence is not liable to form polymer–solvent compounds.

Acknowledgment. X.H. is indebted to the government of the People's Republic of China for a grant in aid.

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Low-Temperature Soluble-Type Sol–Gel Transition in a Newly Synthesized Poly(organophosphazene) and Water System

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Received April 1, 1988; Revised Manuscript Received August 20, 1988

ABSTRACT: A poly(organophosphazene) bearing ethylamino, ethoxy, and hydroxyl groups as its side chains has been newly synthesized by the ring opening/substitution method developed by Allcock. The contents of these groups are 12.4 mol % NHC_2H_5, 41.9 mol % OC_2H_5, and 45.7 mol % OH. This polymer was soluble in water at low temperature, and the solution thus prepared was transformed to its gel state on heating and returned to the sol state on cooling. We termed this thermoreversible transition low-temperature soluble (LTS) type sol–gel transition. The molecular structure was determined by elemental analysis, infrared spectroscopy, ^{31}P nuclear magnetic resonance (NMR), and differential scanning calorimetry (DSC) measurements. The sol–gel transition behavior is discussed by relating the behavior to the molecular structure. The low-temperature solubility and the phase separation at high temperature were due to the balanced structure of the hydrophilic groups and the hydrophobic ones. The gel could be formed by hydrogen bonding among the side chain groups. The synthetic mechanism is also discussed by relating the mechanism to the high reactivity of the P–Cl bond and the synthetic pathway.

Introduction

Most solutions of synthetic linear polymers in a variety of organic solvents, some of which are prepared at elevated temperatures, thermoreversibly undergo gelation on cooling and solation on heating. This may be termed ordinary or high-temperature soluble (HTS) type sol–gel transition. However, a poly(organophosphazene) we have synthesized showed extraordinary low-temperature soluble (LTS) type sol–gel transition in aqueous solution; heating caused gelation and cooling caused solation. It should be noted that the transition was reversible with temperature change. This extraordinary temperature dependence prompted us to study the reversible sol–gel transition using this new polymer system.

In previous studies of sol–gel transition of isotactic poly(4-methyl-1-pentene) (P4M1P),[1] we indicated the structure and dynamics of gels of crystallizable polymers. The peculiar morphology and the polymorphism of the P4M1P crystal are the useful keys to analyze the gel structure. However, that the crystal structure is used for characterization of gels may rarely be the case. The crystallization behavior must still be considered to confuse the characterization of many polymeric gels. Tan et al. discussed the thermoreversible sol–gel transition on atactic polystyrene(aPS)–solvent systems.[2] For the uncrystallizable nature of aPS, the true nature of the transition behavior could be more clearly observed than for the cases of the other polymers and characterized by relating it to the temperature–concentration phase diagram. As shown by these two cases, the peculiarity of the polymers was useful for characterization of gels. The low-temperature solubility of our polymer must also be a utilizable characteristic to understand the polymeric gels.

Poly(dichlorophosphazene), $(-N{=}PCl_2-)_n$, is unstable in water due to the hydrolysis of the Cl—P—Cl bonds. This is one reason why this compound was not practically used until Allcock found a modification method.[3-5] By his method, the Cl–P–Cl bonds were replaced with a variety of organic nucleophiles to yield water-stable poly(organophosphazenes). A large number of poly(organophosphazenes) have been synthesized by Allcock and other groups.[6-24] So far as we know, almost all of them were synthesized for the purpose of replacing all the chlorine atoms with organic groups. And even for the preparation of a water-soluble poly(organophosphazene), the methylamino group was partly introduced as the cosubstituent.[7] When one P–Cl bond of the Cl–P–Cl bonds is replaced with an organic group R, the remaining P–Cl bonds are easily hydrolyzed but the resulting R–P–OH is stable in water.[6] From this fact, we expected that the one-sided

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