cantly lowers T_c as shown in Table III and in Figures 5–9.

(36) This assumption is used only when we qualitatively discuss the concentration dependence of ϕ_{calcd} and the spatial packing of the spherical domains but not when we discuss the temperature dependence of the segregation power and its effect on microdomain structure.

(37) The segregation power between the constituent block chains gradually decreases with increasing temperature, which should result in a gradual "disappearance" of the microdomain structure as will be described typically by eq 21. However, the gradual decrease of the segregation power induces the lattice disordering at $T \sim T_d$ and eventually the dissolution of the microdomains at $T \sim T_c$.

(38) **Note Added in Proof.** Alternatively eq 13 may be interpreted in terms of conformational entropy. A simple deswelling process according to eq 12a results in a strong loss of conformational entropy of polybutadiene chains emanating from the polystyrene spheres due to a decreased volume available to these chains. This loss of entropy is avoided by expanding the size of the spherical domain size because it results in the expansion of the interdomain distance and hence in increasing the volume available to the polybutadiene chains.

Thermoreversible Gelation of Atactic Polystyrene Solutions

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ABSTRACT: Atactic polystyrenes (aPS) with either narrow or broad molecular weight distributions have been found to exhibit thermoreversible gelation in a large number of solvents. Samples with molecular weights from 4×10^3 to 2×10^6 were capable of gelation. Clear, one-phase gels were generally formed above the upper critical solution temperature (UCST); below UCST the gel became turbid, i.e., two-phase. No difference was observed between the gelation (T_{GL}) and melt (T_m) temperatures. At relatively low polymer concentrations microsyneresis occurred, implying a volume contraction. A concentration below which no gelation occurred, termed the critical gel concentration (CGC), was a characteristic of each molecular weight. The dependence of CGC on the molecular weight suggests that chain overlap is a necessary condition for gelation. The sol–gel transition temperature could not be correlated with the polymer–solvent interaction parameter. At present, it appears that specific solvent–polymer interactions are necessary for the onset of gelation. The length of the polymer chain and the molecular structure of the solvent affect the ease of gel formation and gel stability.

Introduction

A polymer gel is a three-dimensional network of flexible chains cross-linked by chemical or physical bonds. Accordingly, gels are classified into two types: irreversible and reversible, respectively. In the latter case, any physical process that favors association between certain sites on different chains may lead to gel formation. In a recent review,[1] de Gennes defines three main possibilities as physical gel-forming agents. One possibility is the presence of helical structures with two or more strands entwined to produce the cross-links necessary for network formation. Formation of microcrystallites, which are incapable of excessive growth, represents a second possibility. A third possibility involves the association of like segments of a copolymer dissolved in a solvent that is good for one segment and poor for the other. This latter association may result in nodular, rodlike, or lamellar cross-linking structures. Although assigning one of these types of associations to a particular gel system is still disputed, the fact remains that a mechanism of physical cross-linking is a necessary requirement for thermoreversible gel formation.

More inclusively, these systems are classified by Flory[2] as polymer networks formed through physical aggregation. The aggregates are seen as predominantly disordered but with regions of local order. From the universal characteristics of all types of gels, Flory infers that they must possess a continuous structure of some sort. None of these theories concerned with the nature of the physical aggregations involved in network formation accounts for the previously observed gelation of aPS.[3] This polymer is not known to possess any of the commonly accepted gel-forming characteristics.[1,2] Controversial questions are thus raised regarding possible local order and the origin of associative interchain interactions of the amorphous macromolecule in its solution, gel, or glassy state.

Table I
Molecular Weight Characteristics of Atactic Polystyrene Samples

$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	lot no.	source
2.0×10^6	<1.2	14B	Pressure Chemical Co.
9.6×10^5	<1.06		Polymer Laboratory Ltd.
6.7×10^5	<1.15	13A	Pressure Chemical Co.
4.1×10^5	<1.06	300-2	Arro Laboratories, Inc.
2.65×10^5	<1.05		Polymer Laboratories, Inc.
2.0×10^5	<1.06	1C	Pressure Chemical Co.
9.7×10^5	<1.06	4A	Pressure Chemical Co.
3.0×10^4	<1.05		Polymer Laboratories, Inc.
2.0×10^4	<1.1		Polymer Laboratories, Inc.
4.0×10^3	<1.1	11B	Pressure Chemical Co.
2.794×10^5	3.08	DF60915	Dow Chemical Co.

This work concerns the characterization of thermoreversible gelation in aPS solutions. Molecular weight and solvent effects have been considered. At present, because there is no unequivocal explanation for the observed phenomena, the subject is presented in the form of a somewhat detailed question in the hope of stimulating future research into the fundamentals of the macromolecular "structure" in the "amorphous" state.

Experimental Section

A. Materials and Procedure. Narrowly dispersed and polydispersed polystyrene with molecular weights in the range 4 ×

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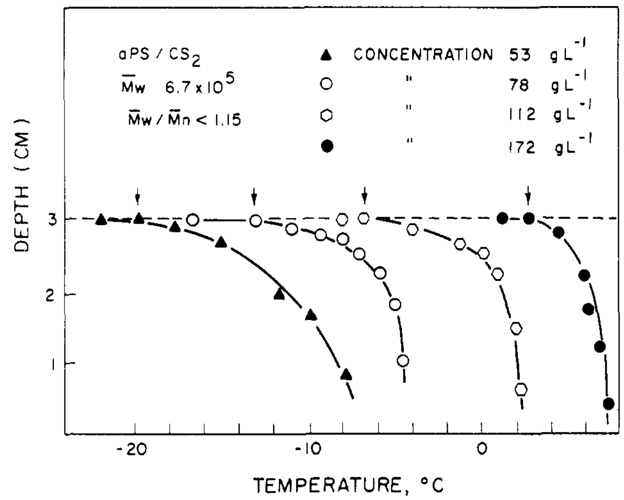

Figure 1. Illustration of the ball-drop method. Arrows indicate melt temperatures of gels formed from aPS/CS_2 solutions of various concentrations.

10^3 to 2×10^6 was obtained from several commercial sources (Table I) and stored in a desiccator over phosphorus pentoxide. Solvents were generally reagent grade and distilled prior to use.

Gels were prepared by dissolving the polymer at room temperature in a suitable solvent at the desired concentration (grams/liter) in a sealed tube and cooled slowly. The refrigerant was either a dry ice–acetone mixture (to -70 °C) or liquid nitrogen (to -150 °C).

Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer differential calorimeter, Model DSC-2. The heating rate was generally 10 °C min^{-1}. Indium was used for calibration (T_m = 156.6 °C, ΔH_f = 28.45 J g^{-1}). The general procedure for sample analysis was to pipet about 10 mg of an aPS solution into liquid pans, which were then sealed tightly.

B. Determination of Sol–Gel Transition. Two methods were used to determine the gelation and melting temperatures: test tube "tilting"[3] and the ball-drop method.[4] In the first method, the gelation temperature was determined by tilting the test tube containing the solution. The temperature at which the solution no longer flowed was taken as the temperature of gelation (T_{GL}). In the second method, a steel ball was placed on the top of the gel (all gels prepared were capable of supporting a steel ball). The temperature was allowed to rise at a suitable rate (usually less than 1 °C/min) and the depth of the steel ball recorded as a function of temperature. The point at which the depth–temperature curve deviated from horizontal (arrows in Figure 1) was taken as the gel melting temperature (T_m). Measurements of T_m obtained by the two methods were identical within an experimental error of ±2 °C.

Results

A. General Features of Atactic Polystyrene Gels. Stable thermoreversible gels were obtained from all molecular weight polymers investigated (Table I) in a large number of solvents. As the temperature was lowered, gels formed from relatively dilute solutions exhibited syneresis followed by phase separation as indicated by turbidity. In general, gels formed outside the binodal region were clear, and those formed within the binodal region were turbid. Once formed, the gels were insoluble in an excess of the same solvent. The gelation temperature (T_{GL}) and gel melting temperature (T_m) of aPS gels are identical, in contrast to thermoreversible gelation of crystallizable polymers. Gels aged for 2 weeks remained transparent and there was no change in the melting temperature. When the rate of cooling was increased from 0.8 to 15 °C/min, essentially no change was observed in the gelation temperature.

Phase diagrams for solutions of various molecular weight polymers in different solvents were established. The phase diagrams are plotted in a plane of reduced temperature $[(T - \Theta)/\Theta]$ vs. concentration. Figure 2 depicts the phase diagram of a narrowly dispersed molecular weight polymer ($\bar{M}_w = 3.0 \times 10^4$) dissolved in CS_2. This figure typifies phase diagrams of aPS in many solvents. The Θ temperature in this system (Θ = 200 K) was estimated by Flory's method[5] from the molecular weight and the upper critical solution temperature (UCST). Above the binodal curve, a one-phase region exists. The one-phase region is further divided by the sol–gel transition curve into two parts: one-phase sol (i) and one-phase clear gel (ii).

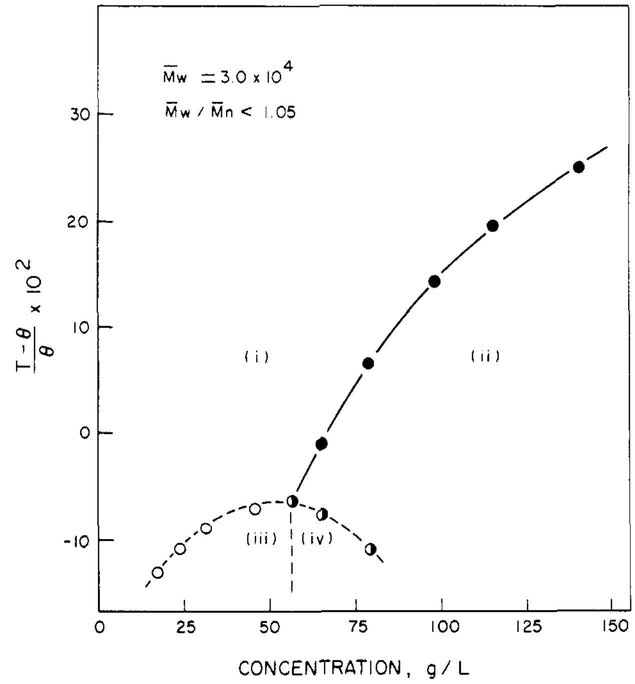

Figure 2. Phase diagram of a narrowly dispersed aPS ($\bar{M}_w = 3.0 \times 10^4$) in CS_2 showing four phases: one-phase solution (i), one-phase gel (ii), two-phase solution (iii), and two-phase gel (iv).

As shown in Figure 2, a solution containing 65 g/L polymer (or more) formed a clear gel in the area (ii) of the phase diagram, i.e., at and below the sol–gel transition curve. When this solution was cooled further, it exhibited phase separation at and below the binodal boundary; thus the clear gel was transformed to a turbid gel. On the other hand, a clear (one-phase) solution containing 56 g/L polymer transformed directly into a turbid (two-phase) gel upon crossing the binodal. Solutions with lower polymer concentrations did not form gels. This concentration, 56 g/L in the system in Figure 2, is defined as the "critical gel concentration" (CGC). A vertical projection of CGC divides the area under the binodal into two parts; turbid (two-phase) solution (iii) and turbid (two-phase) gel (iv).

B. Molecular Weight Effects. The vertical displacement of the binodal curve from the Θ temperature line, the width of the binodal curve, and the shape of the sol–gel transition curve were strongly dependent on the molecular weight and molecular weight distribution of the polymer. The gelation behavior of the polydisperse aPS/CS_2 system is compared with two narrowly dispersed polymers, one of a similar weight-average molecular weight (solid circles) and the other of similar number-average molecular weight (solid diamonds), in Figure 3. The narrow fraction with the same weight-average molecular weight exhibits the sol–gel transition at higher temperatures and has a lower CGC compared to the polydisperse system. On the other hand, the polymer with a similar number-average molecular weight shows very close gelation behavior, i.e., almost identical sol–gel transition temper-

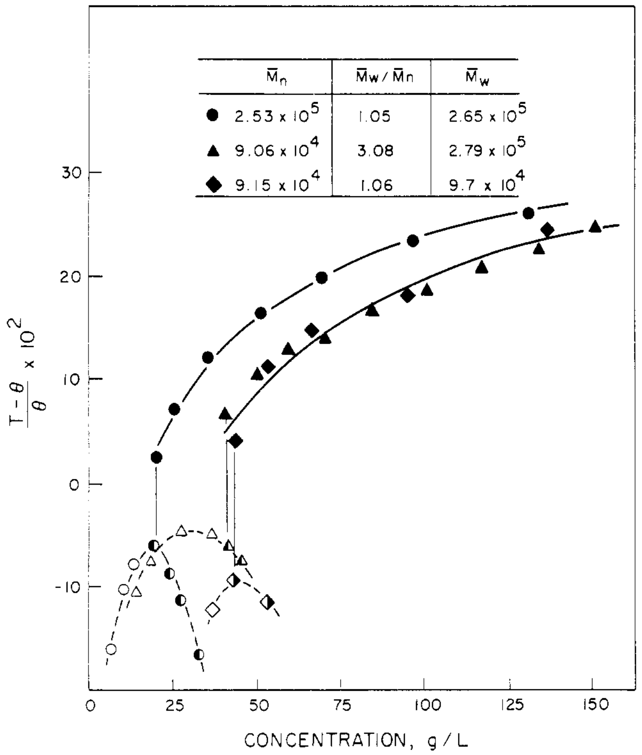

Figure 3. Effect of molecular weight dispersity on the phase diagram of the aPS/CS_2 system.

atures and CGC. All three polymers show different binodal curves. It is interesting to note that the gelation curves in Figure 3 do not intersect the binodal. The vertical projection of the CGC sometimes, but not always, intersects the binodal at the upper critical solution point.

The effect of molecular weight is further described in terms of the sol–gel transition, i.e., the curve separating phases i and ii of Figure 2. Figure 4 exhibits the gelation temperature–concentration relationship of narrowly dispersed molecular weight polymers dissolved in CS_2. Of major significance is the observation that all molecular weights were capable of gel formation. The lowest concentration at which a particular polymer was capable of forming a one-phase gel (CGC) was a unique characteristic of each molecular weight.

C. Solvent Effects. Gelation of aPS in a large number of solvents has been attempted. At present, only 14 liquids, most of them relatively poor solvents, have been found capable of gel formation. Most of the gelling solvents show the same type of phase behavior as the aPS/CS_2 system. The phase diagram of aPS in nitropropane is shown in Figure 5. The binodal is broader than in CS_2 and shifted to higher polymer concentrations. The gelation curve intersects the binodal above the upper critical solution concentration and a continuous gelation curve across the binodal regime is observed. At a concentration of about 100 g/L, the upper critical solution concentration, a much less temperature-dependent gelation is observed. At concentrations below 100 g/L, the system exhibits definite microsyneresis, which results in the insignificant concentration dependence of the gelation temperature. It is interesting to note that a turbid gel can be formed either from a turbid solution or from a clear gel. Upon cooling a one-phase solution containing 190 g/L or less of aPS in nitropropane, the solution first becomes a two-phase turbid solution which transforms into a two-phase turbid gel. On the other hand, a one-phase solution of about 268 g/L forms a one-phase gel, which then becomes a turbid gel when cooled further.

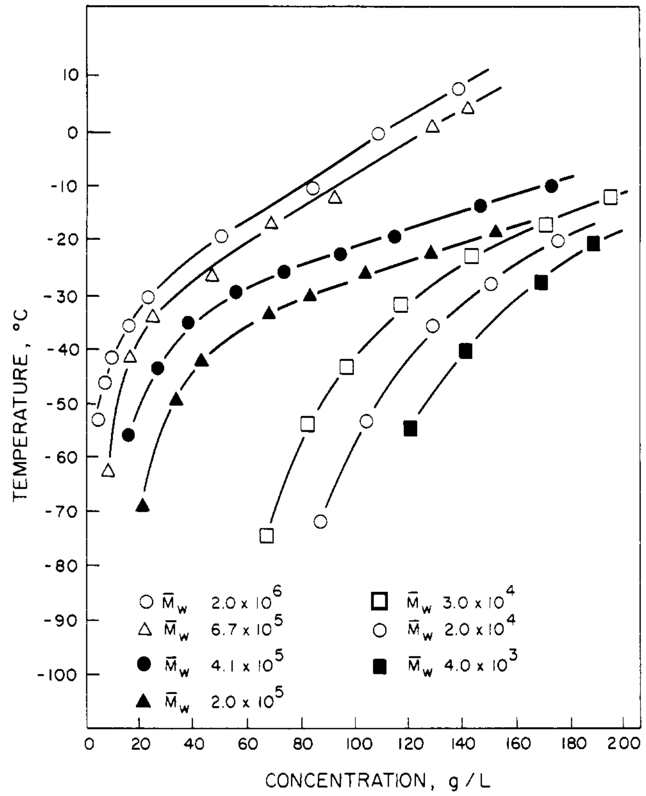

Figure 4. Dependence of the sol–gel transition temperature on the polymer concentration for various narrowly dispersed molecular weights. The lowest concentration indicates CGC.

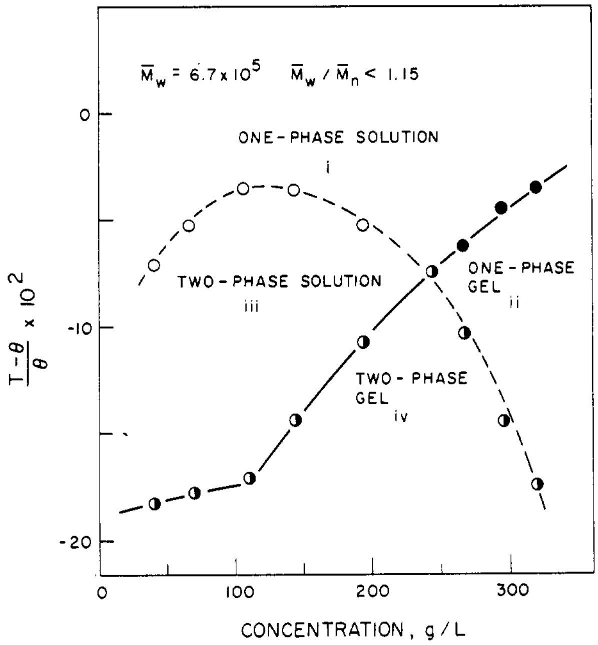

Figure 5. Phase diagram of a narrowly dispersed aPS ($\bar{M}_w$ = 6.7 × 10^5) in nitropropane.

Figure 6 shows the sol–gel transition curves of 6.7 × 10^5 molecular weight polymer in a number of selected solvents. All these solvents formed clear gels. With the exception of CS_2, CGC coincides with the freezing point of the solvent. The sol–gel transition at higher concentrations is strongly dependent on the type of solvent used. Figure 7 summarizes the gelation temperature–concentration relationships of this polymer in two series of solvents: aliphatic acetates and monochloroalkanes. These solvents were capable of forming clear gels and turbid gels (dashed lines) as well. The monochloroalkanes formed clear gels

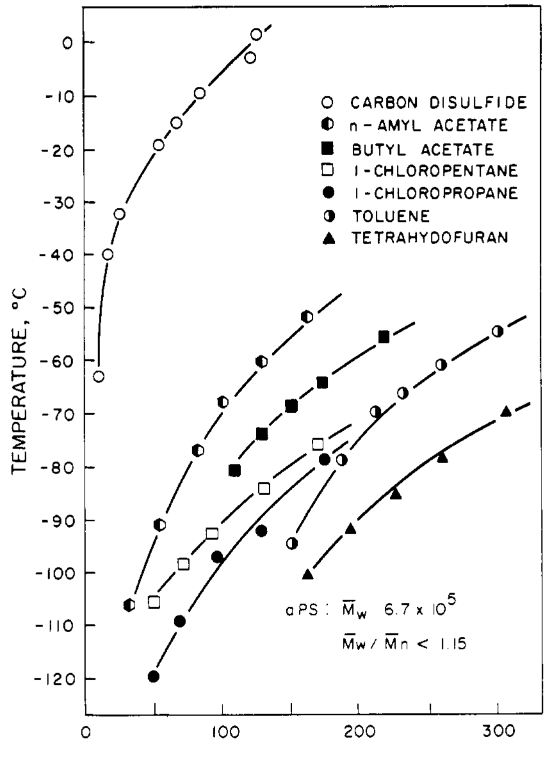

Figure 6. Gelation behavior of aPS ($\bar{M}_w$ = 6.7 × 10^5) in selected solvents.

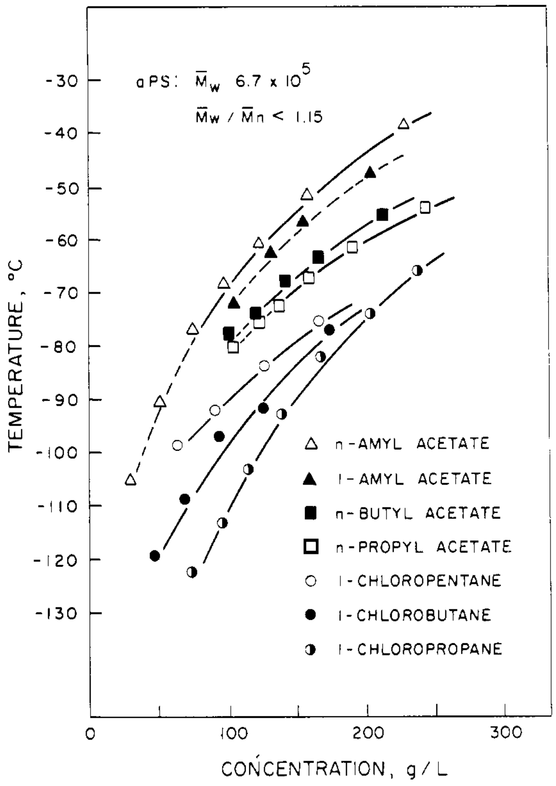

Figure 7. Gelation behavior of aPS ($\bar{M}_w$ = 6.7 × 10^5) in aliphatic acetates and in chloro paraffins. Solid lines indicate one-phase (clear) gels and dashed lines indicate two-phase (turbid) gels.

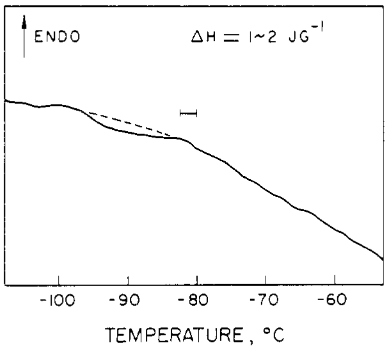

Figure 8. DSC scan of a 160 g/L solution of aPS ($\bar{M}_w$ = 9.6 × 10^5) in toluene. The bar indicates the gelation temperature determined by the tilted test tube method.

while the acetate series formed gels from turbid solutions (cf. Figure 5). The transition from clear to turbid gel depends on the solvent; for example, gels from isoamyl acetate solutions were turbid at all concentrations examined but the other acetates formed clear gels at the higher concentrations. Unlike nitropropane, the acetate system did not exhibit syneresis, and the T_{GL} decreased continuously with decreasing polymer concentration. Generally, in each of the two families of solvents, for a fixed polymer concentration, T_{GL} increased with increasing molecular size of the solvent.

High-sensitivity calorimetric measurements were carried out with a DSC-II to evaluate the heat associated with the sol–gel transition. Figure 8 shows a DSC cooling scan of a 160 g/L toluene solution of a $\bar{M}_w$ = 9.6 × 10^5 aPS. A transition was detected at about −80 °C, which corresponds to the gelation temperature of the same solution as measured by the tilted test tube method. From the exotherm associated with this transition, a heat of gelation on the order of 1–2 J/g was calculated.

Discussion

Atactic polystyrene has been observed to undergo thermoreversible gelation in a number of different solvents. The gel state of aPS appears to be an equilibrium state. This is indicated by the experimental observation of $T_{GL} = T_m$ and by the absence of any detectable time-dependent phenomena.

The phase diagrams of Figures 2 and 5 display the general qualitative features of the phase diagram proposed by de Gennes[1] for a chemically gelating system in a semidilute solution with a good solvent. They also share some general characteristics of the phase behavior suggested by Daoud and Jannink.[6] The phase diagrams of aPS indicate that gelation occurs as a distinct transition and that the phenomenon is not caused by, although related to, phase separation. In most of the gel-forming solvents, clear, one-phase gels are formed at temperatures above the binodal curve. In some cases, the gelation curve intersects the binodal. Solvents such as nitropropane and isoamyl acetate, in contrast to the other solvents, are characterized by gelation at temperatures below phase separation whereby a turbid gel is observed. The coexistence of the gel with phase separation is evident from the observation of turbid gels (area iv in Figures 2 and 5) below the binodal curve. The fact that the turbid gel formed in area iv retains its elastic properties indicates that it consists of a polymer-rich phase dispersed in the continuous gel phase.

The binodal curve is described in terms of the theories of polymer solutions.[5-7] Gelation behavior is also determined by polymer–solvent interactions but does not correlate in a simple way with the binodal curve. Unfortunately, no satisfactory theoretical treatment of the sol–gel transition as observed in noncrystallizable polymers has been proposed.

Gel formation does not appear to be synonymous with the glass transition of the highly plasticized polymer. The glass transition of CS$_2$-plasticized atactic polystyrene was shown by Jenckel and Hensch[8] to be described by the Gordon–Taylor equation, with the glass transition of CS$_2$

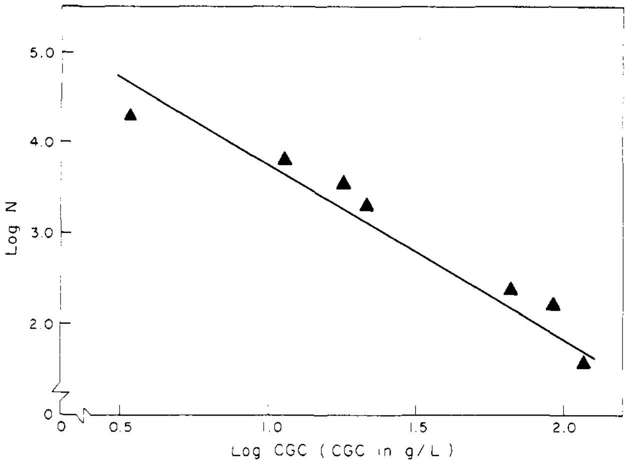

Figure 9. CGC of aPS/CS_2 as a function of N, the number of monomer units in the chain. The solid line has the theoretical slope of −2.

at −175 °C. The calculated glass transition of solutions in the concentration range investigated here would be more than 100 °C lower than the observed gelation temperature. The sol–gel transition may be related to the crossover from repulsive to attractive interactions in the semidilute region of the phase diagram of Daoud and Jannink,[6] but this approach, and others, needs further investigation.

Insight into the nature of network formation in an atactic polymer solution is gained by examination of the role played by the molecular weight and its distribution. Polymers with similar number-average molecular weight exhibit identical gelation behavior, irrespective of their dispersity (Figure 3). This implies that the chain length determines the ease of gelation (T_{GL}) and consequently the stability of the gels formed in any given solvent. Presumably, the low molecular weight end of the polydisperse polymers remains in solution at the sol–gel transition and hence exerts no effect on the gelation behavior.

The critical gelation concentration (CGC) is strongly dependent on the molecular weight. This is shown with the aPS/CS_2 system. Only this system gelled at temperatures high enough that solvent freezing did not interfere with determination of CGC. These results have been analyzed in terms of the concept of chain overlap. The critical concentration C_* at which quasi-ideal coils begin to overlap the pervaded volume of one another is related to the molecular weight as

$$N = KC_*^{-2} \qquad (1)$$

where N is the degree of polymerization and K is a constant.[6,9,10] The critical concentration C_* is identified as CGC, and Figure 9 expresses the CGC data from Figure 4 in terms of the above relationship. The straight line with a slope of −2 fits the experimental results for all molecular weights. This result supports the idea that chain overlap is a necessary condition for network formation and gelation. In view of the fact that gelation occurs only in certain solvents, a specific solvent–polymer interaction, yet to be defined, is also required for the observed gelation phenomenon.

Like gels formed from solutions of crystallizable polymers, the gel stability and hence the gel melting points depend on polymer concentration and molecular weight. This effect has been analyzed for crystallizable systems[11-14] in terms of the relationship proposed by Ferry and Eldridge[11]

$$\ln C = \text{constant} + \Delta H_m/RT_m \qquad (2)$$

for constant molecular weight, where C is the polymer concentration. Relationship 2 was obtained by applying the van't Hoff isochore to an assumed equilibrium between actual and potential network junctions in the gelling solution. The enthalpy change (ΔH_m) in relationship 2 represents the heat absorbed to form a mole of the junction points that stabilize the network structure of the gel.

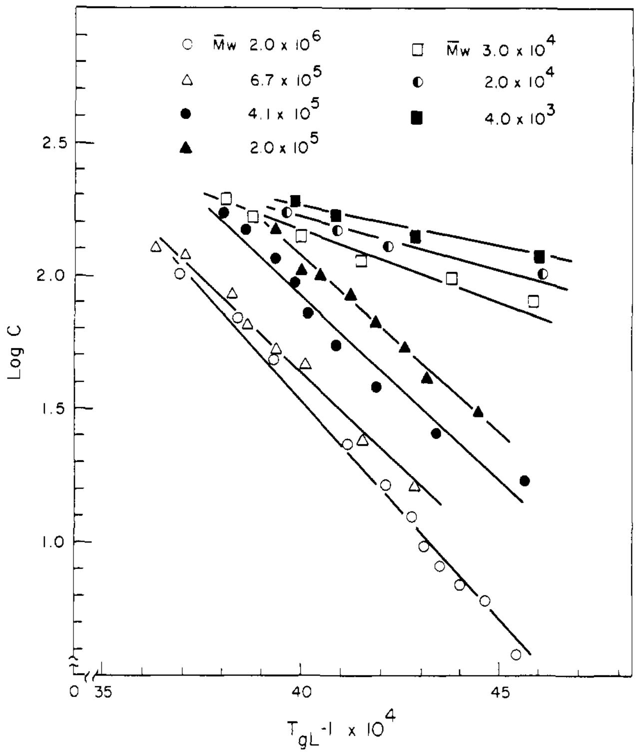

Figure 10. Dependence of $1/T_{GL}$ on log C for polymers of various molecular weights in CS_2.

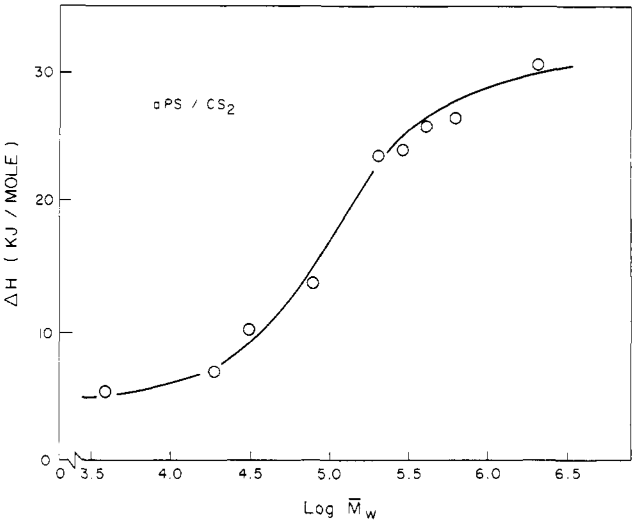

Figure 11. Dependence of the gelation enthalpy obtained from Figure 10 on the molecular weight of the polymer.

When the reciprocal of the gelation temperature in CS_2 is expressed as a logarithmic function of concentration, the data for each molecular weight fit a straight line (Figure 10). The slope yields a value of ΔH_m that increases with increasing molecular weight. The dependence of ΔH_m obtained from Figure 10 on the molecular weight is shown in Figure 11. Since the applicability of the underlying assumptions of the Eldridge–Ferry analysis to aPS gels is not yet confirmed, ΔH_m is simply considered as an enthalpy difference associated with the sol–gel transition.

Gel stability, as indicated by the gelation enthalpy, varies from one solvent to another. The gelation enthalpies

Table II
Gelation Enthalpy of aPS in Various Solvents[a]

	solubility parameter, (cal/cm^3)$^{1/2}$	interaction parameter χ	gelation enthalpy, kJ/mol
carbon disulfide	10.0	0.40	26.3
n-amyl acetate	7.8	0.48	11.7
isoamyl acetate	8.5		11.4
n-butyl acetate	8.5	0.48	10.6
n-propyl acetate	8.8		10.6
1-chloropentane	8.3		12.2
1-chlorobutane	8.1		8
1-chloropropane	8.1		5.8
MEK	9.3	0.47	8.5
toluene	8.9	0.44	9.5
THF	9.1	0.38	6.9
nitropropane	10.3		11.7
methylene chloride	9.7		no gel
chloroform	9.3	0.42	no gel
carbon tetrachloride	8.6	0.48	no gel
1,2-dichloroethane		0.47	no gel
trichloroethane	9.2		no gel
p-dioxane	10.0	0.46	no gel
cyclohexane	8.2	0.505	no gel
benzene	9.2	0.45	no gel
aniline	10.3		no gel
benzaldehyde	9.4		no gel
nitrobenzene	10.0		no gel
Decalin	8.8		no gel

[a] $\bar{M}_w = 6.7 \times 10^5$.

Table III
Gelation of aPS in Various Solvents[a]

solvent	mp, °C	molar volume	T_{GL}, °C	ΔH, kJ/mol
n-amyl acetate	−100	148.6	−52	11.7
isoamyl acetate	−78	148.6	−56	11.4
n-butyl acetate	−78	131.7	−65	10.6
n-propyl acetate	−95	114.9	−68	10.6
1-chloropentane	−99	120.7	−76	12.2
1-chlorobutane	−123	104.5	−79	8.0
1-chloropropane	−123	88.1	−86	5.8

[a] 166 g/L, $\bar{M}_w = 6.7 \times 10^5$.

of aPS in all the solvents investigated are summarized in Table II. The highest gelation enthalpy was observed for CS_2, 26 kJ/mol, for the molecular weight used in the comparison. Gelation enthalpies in other solvents are much lower, ranging from 6 to 12 kJ/mol. The unusual stability of the CS_2 gels is also apparent from the relatively high melting temperature of these gels.

Systematic changes in gel stability are observed within a series of chemically similar solvents. In Table III the gelation enthalpies and gelation temperatures for solutions of one concentration (166 g/L, $\bar{M}_w = 6.7 \times 10^5$) in two solvent series are listed together with the molar volume and freezing point of the solvents. Within each series, it is observed that the gel stability increases with increasing molar volume of the solvent. There does not appear to be any correlation between gel stability and the melting point of the solvent.

Measures of the goodness of a solvent such as the Flory–Huggins interaction parameter or the Hildebrand solubility parameter might be expected to correlate with gelation enthalpy. Some of these parameters[15,16] are also listed in Table II with the corresponding gelation enthalpies. There appears to be no simple correlation. A similar finding has been recently reported in a study of PVC gelation in various solvents.[12] It may be inferred here that solvent–polymer interactions play a critical role in the creation of network junctions. In other words, whether the system will gel or not appears to be ultimately determined by a specific interaction parameter which is as yet unknown. On the basis of the experiments described here, it is reasonable to suggest that gel formation involves both chain overlap and a mechanism of network stabilization. The latter is, at present, not understood. It may involve chain stiffening or attractive associations of chain segments.

Table IV
Comparison of Gelation Enthalpies of Various Polymers

polymer/solvent	$\bar{M}_w$	$\bar{M}_n$	ΔH, kJ/mol
aPS/CS_2	2.0×10^5	1.9×10^5	24.7
	3.0×10^4	2.9×10^4	10.4
iPS/Decalin[17]	5.15×10^5	5.1×10^4	113
PVC/1,4-dioxane[12]	1.33×10^5		45.0
	5.6×10^4		36.0

It is of interest to consider briefly the implications of the gelation of a noncrystallizable polymer to the well-known gelation phenomenon of crystallizable polymers. The gelation of aPS solutions shows the same dependence on concentration as gelation of crystallizable polymers. This suggests that there exists a common gelation mechanism. The values of gelation enthalpy calculated from eq 2 for aPS are compared in Table IV with values for iPS and PVC gels calculated in the same way. The gelation enthalpies of aPS are smaller than those of crystallizable polymers but of the same order of magnitude. Unlike aPS gels, PVC and iPS gels undergo aging processes that involve crystallite growth. One possibility is that the higher enthalpy of PVC and iPS gels is associated with gel stabilization by crystallization, but the underlying mechanism of gel network formation is the same or very similar for both crystallizable and noncrystallizable polymers.

Conclusions

A noncrystallizable polymer, atactic polystyrene, has been shown to undergo thermally reversible gelation in certain solvents. These gels show the following characteristics:

(1) The gelation is an equilibrium process in that the temperatures of gel formation and gel melting are the same. The properties of aPS gels do not appear to change with time.

(2) Each molecular weight is characterized by a critical gelation concentration (CGC) below which the system will not gel. The inverse square dependence of CGC on molecular weight suggests that chain overlap is a necessary condition for gel formation.

(3) Values of the gelation enthalpy calculated from van't Hoff type plots indicate that aPS gels are somewhat less stable than gels of crystallizable polymers. It is suggested that the mechanism of gel formation in aPS may also be involved in gelation of crystallizable polymers.

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Registry No. Polystyrene, 9003-53-6.

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Determination of Gel Content and Percent Gel in Radiation-Cured Poly(vinyl chloride)–Cross-Linking Monomer Coatings by Combined GPC–LC Techniques

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ABSTRACT: A GPC–LC technique for determining gel content and monomer and polymer content of the gel as well as molecular parameters for ungelled polymer is outlined for use with monomer–polymer mixtures. The method is applied to mixtures of poly(vinyl chloride) (PVC) and trimethylolpropane trimethacrylate (TMPTMA) and three-component mixtures also containing diundecyl phthalate (DUP) plasticizer. All were cured by electron irradiation. Comparison to the conventional Soxhlet extraction technique and gravimetric analysis reveals that gel content for these PVC mixtures is more accurately measured by the GPC–LC technique. The influence of temperature and extraction time are shown to be very important in accurately determining gel content by the GPC method. Precision is aided by using an internal standard. Data obtained are useful in mechanistic studies and correlations of physical and mechanical properties with molecular changes.

Introduction

The determination of gel content for polymers and cross-linked monomer–polymer mixtures and blends provides data by which physical and mechanical properties can be related to the molecular property changes. Generally, such a determination is made by weighing the gel remaining after all soluble components have been removed by solvent extraction.[1] Extraction is accomplished by Soxhlet techniques using hot solvent or by long-term shaking or rapid stirring in a suitable solvent at room temperature. The technique of Purdon and Mate[2] as modified by Rogozinski and Kramer[3] affords a highly accurate means for determining gel content in poly(vinyl chloride). Its drawbacks are the considerable length of time required before data are obtained and the multiplicity of steps needed. These include dissolution, filtration, centrifugation, and drying of polymer recovered. Soxhlet extraction avoids the physical filtration and centrifugation steps. However, it suffers from the single operating temperature demanded by refluxing solvent and the drying process.

Recently, a more simple technique employing gel permeation chromatography (GPC) was applied to gel content analysis of polymers. The first workers[4] analyzed nitrile rubber latexes by directly injecting the latex onto a GPC column. Results were very good for >30% gel content and analysis times were very short (20–30 min). Correspondence of data between standard static analysis and the GPC method was good.

More recently, Ezrin and Brown[5] reported a similar technique useful for a variety of polymers. In this case filtration of the polymer–gel solution was done prior to injection on the columns. Gel content was calculated from the GPC peak area, a calibration curve, and the initial concentration of the sample in the elution solvent.

The present paper reports the extension of the two previous GPC methods to the more complicated case of polymer–cross-linking monomer mixtures. The particular case chosen for study was poly(vinyl chloride) (PVC) mixed with trimethylolpropane trimethacrylate (TMPTMA). Details of curing this mixture by electron irradiation were first discussed by Salmon and Loan.[6] Additional GPC columns were used in this study to permit a sufficient separation between the monomer and an internal standard that was added to help minimize errors induced by injection volume changes. To our knowledge this is the first report of the use of an internal standard in gel permeation and liquid chromatography to obtain absolute concentration data for eluents.

Experimental Section

Materials. Poly(vinyl chloride) was obtained from BFGoodrich and had $\bar{M}_w = 1.61 \times 10^5$ and $P = 3.26$. Trimethylolpropane trimethacrylate was obtained from Ware Chemical Corp. Diundecyl phthalate was used as received from Monsanto. UV-grade tetrahydrofuran (Waters) was used in the extraction experiments and as the chromatographic solvent. CCl_4 was used as received from Mallinckrodt.

Apparatus. Irradiation of molded PVC–TMPTMA samples was conducted with a Dynamitron electron beam accelerator using 1.5-MeV electrons. Currents ranging from 0.4 to 1.0 mA were used. Absorbed doses <5 Mrd were applied to the samples. Irradiations were conducted under nitrogen at 21–23 °C.

GPC analyses were performed with the Waters Model 244 liquid chromatograph. Most results were obtained with refractive index detection. For some runs UV detection was used for TMPTMA and PVC to which TMPTMA had grafted. The column set consisted of six μ-Styragel columns having porosities of 10^6, 10^5, 10^4, 10^3, 500, and 100 Å. The latter two columns were necessary to obtain good separation between TMPTMA, a large molecule, and CCl_4, the internal standard, which is small, nonpolar, and spherical. A PDP8 Lab 8/E minicomputer was used for data

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