(11) Lemstra, P. J.; Keller, A.; Cudby, M. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1507.
(12) Specacek, J. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 523.
(13) Aubert, J. H.; Clough, R. L. *Polymer* **1985**, *26*, 2047.
(14) Guenet, J. M.; Lotz, B.; Wittman, J. C. *Macromolecules* **1985**, *18*, 420.
(15) Sundararajan, P. R.; Tyrer, N. J.; Bluhm, T. L. *Macromolecules* **1982**, *15*, 286.
(16) Domszy, R. C.; Alamo, R.; Edwards, C. O.; Mandelkern, L. *Macromolecules* **1986**, *19*, 310.
(17) He, X.; Herz, J.; Guenet, J. M. *Macromolecules* **1987**, *20*, 2003.
(18) He, X.; Herz, J.; Guenet, J. M. *Macromolecules*, **1988**, *21*, 1757.
(19) Mutin, P. H.; Guenet, J. M.; Hirsch, E.; Candau, S. J. *Polymer* **1988**, *29*, 30.
(20) Point, J. J.; Coutelier, C. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 231. Point, J. J.; Coutelier, C.; Villers, D. *J. Phys. Chem.* **1986**, *90*, 3273.
(21) Prud'homme, C. *Thesis*, Strasbourg, 1980.
(22) Flory, P. J. In *Principle of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1951.
(23) Cahn, J. W. *J. Am. Ceram. Soc.* **1969**, *52*, 118.
(24) Schulz, G. V.; Haug, A. *Z. Phys. Chem.* **1962**, *34*, 328.
(25) Feke, G. T.; Prins, W. *Macromolecules* **1974**, *7*, 527.
(26) Toyama, K.; Miller, W. G. *Nature (London)* **1981**, *289*, 813.
(27) He, X. W.; Fillon, B.; Herz, J.; Guenet, J. M. *Polym. Bull. (Berlin)* **1987**, *17*, 45.
(28) Guttman, C. M.; Di Marzio, E. A.; Hoffman, J. D. *Faraday Discuss. Chem. Soc.* **1979**, *68*, 297.
(29) Cahn, J. W.; Hilliard, J. E. *J. Chem. Phys.* **1959**, *31*, 688; **1965**, *42*, 93.
(30) Thirion, P.; Chasset, R. *Chim. Industr.—Gênie Chim.* **1967**, *97*, 617.
(31) Guenet, J. M.; McKenna, G. B. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 2499.
(32) Guenet, J. M. *Macromolecules* **1986**, *19*, 1960.
(33) de Gennes, P.-G. In *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(34) Debye, P.; Bueche, A. M. *J. Appl. Phys.* **1949**, *20*, 518.
(35) Gan, Y. S.; François, J.; Guenet, J. M. *Macromolecules* **1986**, *19*, 173.

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

Tetsuya Tanigami,* Takayoshi Ono, Nobumitsu Suda, Yasuhiro Sakamaki, Kazuo Yamaura, and Shuji Matsuzawa

Faculty of Textile Science and Technology, Shinshu University, Ueda 386, Japan.
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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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hydrolysis of the Cl–P–Cl bonds would be a useful technique to synthesize water-soluble polymers, even though the hydrolysis of the main chain, which necessarily occurs during the synthesis process by this method, must more or less decrease the molecular weight of the polymer. In this work, it was shown that the one-sided hydrolysis method was actually useful for the synthesis of the LTS polymers, when the excess hydrolysis of the main chain could be inhibited.

Experimental Section

Isolation of Ethylamine. Ethylamine was isolated from ethylamine hydrochloride ($C_2H_5NH_2$·HCl). A solution of ethylamine hydrochloride (90 g) in ethanol (300 mL) was added to sodium hydroxide (160 g), and the mixture was then stirred and heated at 60 °C. Volatilized ethylamine was collected into a dry ice–methanol trap through a cooled water condenser (4 °C). The purity of the isolated ethylamine was estimated to be 99%. Ethanol was slightly included. A little inclusion of ethanol was not troublesome in our work, because the chlorine atoms in poly(dichlorophosphazene) were replaced not only by ethylamine but also by ethanol.

Polymerization of Hexachlorocyclotriphosphazene. Hexachlorocyclotriphosphazene was kindly provided by Nippon Soda Co., Japan, and used for polymerization as received. It was a very pure trimer product. Poly(dichlorophosphazene) was prepared by bulk thermal polymerization of hexachlorocyclotriphosphazene. Hexachlorocyclotriphosphazene (43.2 g) was sealed in six Pyrex glass tubes, 18 × 180 mm. The tubes were degassed 3 times by a melt–freeze technique on a vacuum line at 3 mmHg before they were sealed. Polymerization was carried out in a thermoregulated oven at 250 °C for 70 h. The tubes were removed from the oven and cooled at room temperature. The contents were dissolved with benzene and subsequently precipitated in excess *n*-heptane in order to remove the unreacted trimer and oligomers. The operations of isolation of polymer were carried out in a dry nitrogen box to prevent hydrolysis and cross-linking. The yield of soluble, uncross-linked $(—N=PCl_2—)_n$ was 35.7%.

Reaction of $(—N=PCl_2—)_n$ with a Mixed Solution of Ethylamine and Ethanol. A mixed solution of ethylamine (0.27 mol) and ethanol (0.75 mol) was added slowly to a stirred solution of poly(dichlorophosphazene) (15.4 g) in toluene (300 mL). The mole ratios of the two reactants to the chlorine atom in poly(dichlorophosphazene) are 1.0 for ethylamine and 2.8 for ethanol. Volatilized ethylamine was returned to the mixture by means of a condenser cooled by circulating 4 °C water. The reaction was allowed to proceed at 25 °C for 184 h. The reaction mixture consisted of a toluene layer and an ethanolic layer. Into the mixture, 1 N aqueous sulfuric acid was added, and the toluene layer was eliminated. The aqueous layer was kept at room temperature for 1 day to cause hydrolysis of the remaining P–Cl bonds. Hydrolysis on the portion of the Cl–P–Cl bonds in the polymer caused cleavage of the main chain, decreasing the degree of polymerization. The aqueous solution was neutralized with dilute aqueous ammonium hydroxide solution and then dialyzed in distilled water during 1 week. The dialyzed solution was then concentrated. Precipitation of the products was not observed during the dialysis and concentration process. The polymeric solid product was dried in vacuo at 50 °C to remove ethanol. The polymer (14.0 g) was a glassy, transparent product and soluble in water below room temperature.

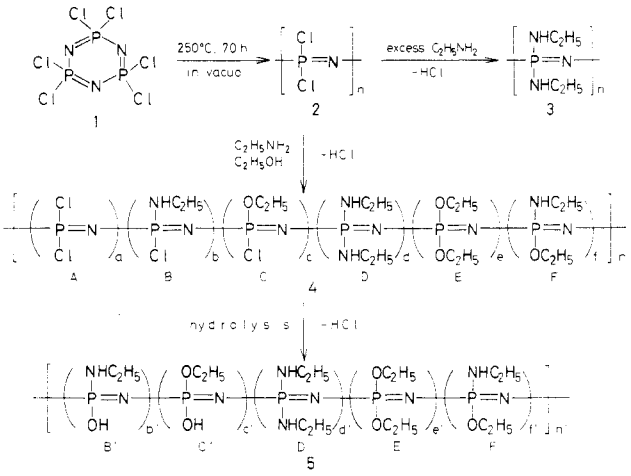
Measurements. ^{31}P NMR spectroscopy was carried out on a Bruker NMR spectrometer at 121.496 MHz. The chemical shift was not referenced to the standard material.

DSC of the dried polymer was carried out on a Rigakudenki TG-DSC unit equipped with a thermogravimetric (TG) analyzer. The sample was heated at 10 °C min^{-1} up to 450 °C.

A membrane osmometry measurement was made on a Zimm-Myerson-type membrane osmometer. An anisotropic permselective membrane of Advantec Toyo, Type 0-0005, was used.

Aqueous solutions of polymer **5** with polymer concentrations between 5.43 and 54.3 g mL^{-1} were prepared for measuring their sol–gel transition points. The polymer and distilled water were sealed in test tubes of 12-mm diameter and 120-mm length and then stored in an ice–water jar for 24 h to dissolve the polymer.

Scheme I



The solution samples were placed in a well-stirred poly(ethylene glycol) bath at 0 °C, and the bath was warmed at a rate of 0.2 °C min^{-1}. The temperature at which clouding was first observed was taken to be the clouding temperature. The temperature at which fluidity of the sample was vanished was taken to be the sol–gel transition temperature.

When the gel sample, c = 54.3 g mL^{-1}, stored at 28.4 °C (T_{gel}) for a given storing time, θ_{gel}, was quickly cooled to a solation temperature of 10 °C (T_{sol}), the induction time for solation, t_{sol}, was measured starting from the cooling time. On cooling, the gel sample was placed upside down. The time at which the gel fell down to the bottom of the test tube was taken to be the solation time.

Results and Discussion

Synthesis and Characterization. When we tried before this work to synthesize poly(bis(ethylamino)phosphazene) (**3**) according to Allcock's method, the same LTS polymer as synthesized in this work was accidentally obtained. After several trials, we found a pathway for the synthesis of the polymer which shows the LTS-type sol–gel transition. The pathway is shown in Scheme I.

If poly(dichlorophosphazene) (**2**) was reacted with more than 4 equiv of pure ethylamine to the chlorine atom of **2**, **3** was produced.[25] In our first trial to get **3**, however, the purity of ethylamine used was quite low. Ethanol used for the isolation of ethylamine as a solvent was accidentally mixed with ethylamine. If the mixed solution of ethylamine and ethanol is reacted with **2**, **4** is yielded. It is known that ethylamine functions not only as the nucleophilic reagent which attacks the phosphorus atoms along the main chain, but also as a catalyst for facilitating ionization of ethanol to ethyl alkoxide.[6] **4** is regarded as a copolymer of six monomers, A–F. Here, we postulate that the hydrolysis of the P–Cl bonds in B and C monomeric units causes no cleavage of the main chain, but that in the A unit causes cleavage of the main chain, as described in the Introduction. Thus, the treatment of **4** with water as described in the Experimental Section yielded **5**. As described above, the chlorines of **2** were replaced with the other groups in two stages: with the ethoxy groups and ethylamino ones in the first stage and with hydroxyl groups in the second stage.

5 was characterized by a combination of elemental analysis, ^{31}P NMR, infrared spectroscopy, and DSC measurements. The mole fractions of the three side chain groups were calculated from the values of C% and N% in elemental analysis data, as Table I shows. The total content of NHC_2H_5 and OC_2H_5 groups which were attached in the first stage of the substitution was almost the same as that of the OH group which was introduced in the

Table I
Elemental Analysis for Polymer 5

	microanalysis			side-chain content, mol %			unit content, mol %				
	%N	%C	%H	NHC_2H_5	OC_2H_5	OH	B′	C′	D	E	F
calcd	16.0	23.9	6.0	12.4	41.9	45.7	23.5	67.5	0.3	8.5	0.2
found	16.0	23.9	5.8								

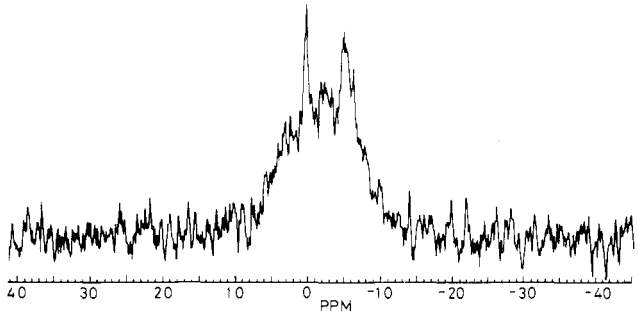


Figure 1. ^{31}P NMR spectrum of 5.

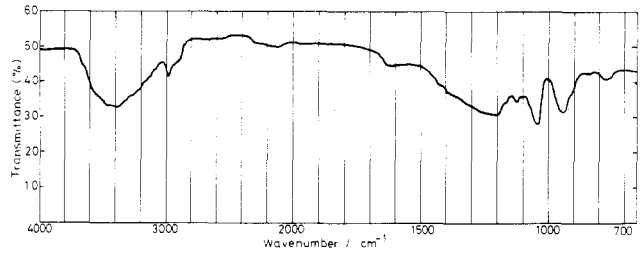


Figure 2. Infrared spectrum of 5.

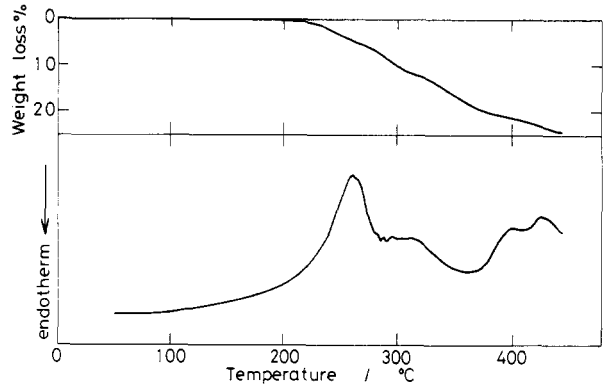


Figure 3. Differential scanning calorimetry and thermogravimetric curves for 5.

second stage and remained in the polymer. Here also attention must be directed to the fact that A units in the chain vanish in the following hydrolysis process. These two facts indicate for the following discussion an important result that 5 can be regarded as a copolymer of B′ and C′ monomeric units. The total content of the two units was 90% as shown in Table I. Comparing the mole ratios of the ethylamine and ethanol reactants to the chlorine atom in 2 in the first stage, the content of the two groups actually attached to 5 was small. Two reasons are considered for this: First, the quantity of the ethylamine reactant used for the substitution was small. Most of ethylamine must act as a hydrochloride acceptor for the replacement of the chlorine with ethanol rather than as the nucleophilic reagent. If ethylamine was excessively added, no chlorine atom should remain in the following hydrolysis stage, and the product may be considered as a copolymer of D, E, and F monomeric units. Second, full replacement with ethanol must be difficult, even if ethanol is excessively added. The secondary attack of ethanol to the phosphorus atom, one of the P–Cl bonds is already substituted by the ethoxy group or the ethylamino one, cannot proceed under our mild reaction condition, because of steric hindrance of the ethoxy group. This was already reported by Allcock.[6] He treated poly(dichlorophosphazene) solution with sodium ethoxide to yield fully substituted polymer with ethoxy groups. On the contrary, the total ratio of the two reactants must not be so low as to increase the number of A monomeric units in 4. If the number is very large, the polymeric product cannot be obtained, owing to the excess hydrolysis of the main chain of 4. The molecular weight by osmometry measurement was 1.94×10^4. The number of monomeric units contained in a polymer chain was calculated to be 178 from this molecular weight.

Figure 1 shows the ^{31}P NMR spectrum of the aqueous solution of 5. As expected from the elemental analysis, the molecular structure is a quite complicated one. Two sharp peaks detected in a broad ground peak must arise from the two main units, B′ and C′. The fine structure which constructs the broad ground cannot be analyzed only with the help of our data. The compounds derived from hexachlorocyclotriphosphazene by substitution reaction with the reactants which we used here must be utilized as the model compounds for analysis of the fine structure. It should be noticed that hydroxyphosphazenes exist as tautomers between OH and NH forms in water.[6] This is also possible in our case and makes the analysis more complicated.

The infrared spectrum of the polymer was fairly well consistent with the expected structure. The spectrum is shown in Figure 2. The principal infrared bands were identified as follows (in cm^{-1}): 3000–3700 (vs. vbr, O—H, N—H), 2980 (m, C—H), 2900 (w, br, C—H), 1430 (vw, P—O—C), 1170–1300 (s, P=N), 1170 (vw, P—O), 1120 (w, C—N), 1050 (s, C—O), 950 (s, P—O). The O—H groups were evident from the very strong, broad peak in the 3000–3700-cm^{-1} region. Within this peak was also to be included the amino N–H peak which was detected as a broad absorption in the 3100–3450-cm^{-1} region.[25]

The dried sample of 5 was a glassy, hard solid. Differential scanning calorimetry coupled with thermogravimetry indicated high thermal stability and noncrystallizable nature of 5 as expected from the molecular structure (Figure 3). Weight loss started at about 200 °C, due to volatilization of the low molecular weight species. The hydrolytic stability of the solid sample remained, even after 3 years of exposure to moisture. Further, 5 was also stable in aqueous solutions. These stabilities are due to the presence of hydrogen bonds between hydroxyl groups and ethylamino ones. The stabilities are more clearly shown when the nature of 5 is compared with that of poly(diethoxyphosphazene) (PBEOP).[6] PBEOP is a elastomer, and its solutions often form gels when stored for long periods of time. The gelation of PBEOP may result from cross-linking.

Sol–Gel Transition Behavior. Figure 4 photographically demonstrates the LTS sol–gel transition of 5. The polymer concentration of the sample used was 54.3 g mL^{-1}. Just as it was taken out of the ice–water jar, the solution, which had been kept at 0 °C for 24 h, was still in a transparent sol state, as the left-side sample shows. Contrary to this, 10 min after the temperature jump from

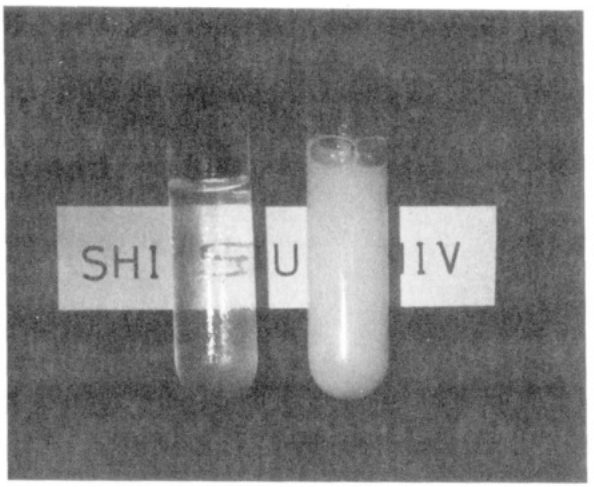


Figure 4. Demonstration photograph of the LTS-type sol–gel transition observed as the temperature jumped from 0 to 30 °C for the sample of c = 54.3 g L^{-1}. The left-side sample, just taken out of a ice–water jar, was still in the sol state. The right-side sample, 10 min after the temperature jump, was in the gel state. It is noted that the sample volume in solution was slightly larger in the right-side sample than in the left-side sample. A foam which was already present only at the interface between the solution and air still remained in the gel state.

0 °C to room temperature (30 °C), the sol–gel transition had already occurred in the sample, as the right-side sample shows. The sample abruptly clouded on transition. Thus, the transition could be visually detected. It should be noted that macroscopic phase separation did not occur in our system. In other words, the gelation in our system was not caused by macroscopic aggregation of precipitates.

When the solution prepared at 0 °C was violently stirred, it foamed, like soap would. This alone indicates that the solubility of the polymer in water is attributed to micelle formation. The molecular structure characterized in the previous section also supports this conjecture. Almost every phosphorus atom in the skeletal chain has a hydrophobic group and a hydrophilic one as the side chains. The ethylamino and the ethoxy groups belong to the former and the hydroxyl group to the latter. At low temperature, the polymer turns the hydrophilic groups to water phase to form the micelle structure. The micelle is destructed on heating, and then association of the polymer causes gelation. Kunieda and Shinoda reported that partially acetylated poly(vinyl alcohol) (PVA-Ac) is a LTS-type polymer in water.[26] And they explained the water solubility of PVA-Ac by relating its molecular structure to the micelle structure. However, liquid–liquid phase separation in the PVA-AC–water system at high temperature caused no gelation, probably because the polymer–polymer cohesion was not so strong to make a three-dimensional network. Recently, we synthesized poly(bis(ethylamino)phosphazene) (PBEAP), whose side chains were almost perfectly occupied by the ethylamino groups, and found that it also has the LTS-type phase diagram in a solution of acetic acid.[25] This polymer was insoluble in pure water and caused no gelation from the acetic acid solution even in the two-phase region. These can be related to the presence of the bulky, hydrophobic ethyl portion which shades the amino portion. Contrary to the above two polymers, the cohesion in our gel must be strong and it can be attributed to the presence of the hydroxyl group whose size is small enough to form hydrogen bonds with the other groups. We did not take the effect of the end groups into consideration for the solubility, because we think that the balanced structure of hydrophobic groups and hydrophilic ones more strongly

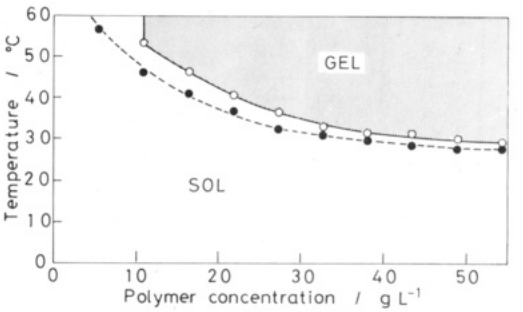


Figure 5. Starting temperature of clouding (●) and sol–gel transition temperature (T_t) (○) observed in a heating process at the rate of 0.2 °C min^{-1}.

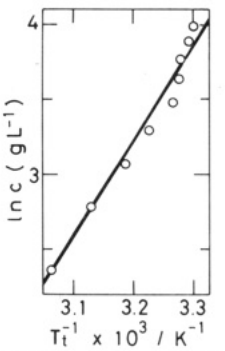


Figure 6. ln c versus T_t^{-1} plot (Ferry–Eldridge plot). T_t values were obtained from Figure 5.

dominates the solubility of the polymer than the end effect.

A partial phase diagram was shown in Figure 5. The sol samples with various concentrations between 5.43 and 54.3 g mL^{-1} had clouding temperatures and sol–gel transition temperatures as shown by empty and solid marks, respectively. These measured values were somewhat overestimated, because the heating rate was high compared with the gelation rate. However, these data lead to valuable information on enthalpy change for the sol–gel transition. Figure 6 shows a ln c versus T_t^{-1} plot for the data in Figure 5. Eldridge and Ferry derived an equation between polymer concentration (c) and sol–gel transition temperature (T_t)[27]

$$\ln c = \Delta H_t / RT_t \tag{1}$$

where the enthalpy change (ΔH_t) represents the heat absorbed to form a mole of the junction points and R is the gas constant. They postulated that the gelation is the formation of three-dimensional networks, infinite in extent, by binary association between linear macromolecules. And the junction is constructed by a number of associations. However, actual structures of many reversible gels, particularly of the crystallizable polymers, are very complicated ones due to secondary structuring in the gel structure, even if the gelation is caused by the molecular association mechanism. It was considered to be unable in these gels to measure the sol–gel temperature (T_t) as a function of the concentration (c), though the melting temperature (T_m) measured as a function of the concentration was analyzed according to a modified equation of (1)[1]

$$\ln c = -\Delta H_m / RT_m \tag{2}$$

where the enthalpy change (ΔH_m) represents the heat absorbed to dissolve a mole of the junction points. In many crystalline polymers, T_t and T_m were essentially different. For thermoreversible gelation without secondary structuring such as crystallization, it may be a necessary condition that the two transition temperatures are equal

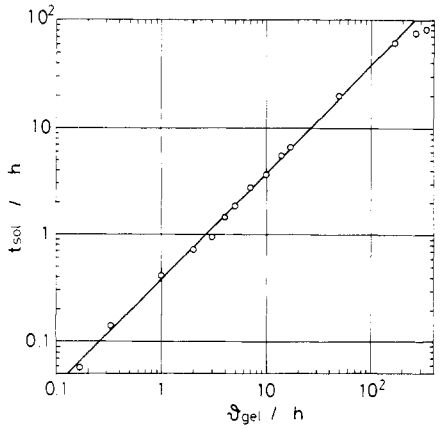


Figure 7. Induction time for solation (t_{sol}) at T_{sol} = 10 °C versus the storing time (θ_{gel}) at T_{gel} = 28.4 °C. The polymer concentration of the sample used was 54.3 g L^{-1}.

to each other. This condition holds true except in the aPS gels investigated by Tan et al.[2] and our LTS gel. The enthalpy change (ΔH_t) calculated from the slope of the line in Figure 6 was 49.0 kJ mol^{-1}. The positive sign of ΔH_t means that the sol–gel transition is an endothermic reaction. The absolute value of ΔH_t is comparable with those reported for an aqueous solution of gelatin.[27]

The solution of the polymer, c = 54.3 g mL^{-1}, was stored for a given period of time (θ_{gel}) at 28.4 °C (T_{gel}), which was close to the sol–gel transition point of 28.0 °C (T_t), and then it was cooled to 10.0 °C (T_{sol}). The time required for solation after the cooling (t_{sol}) was plotted against the storing time, as Figure 7 shows. A linear relationship between the two times was found even at high θ_{gel} region. The slope of the line was 1.0. The relationship between the two times was expressed by

$$t_{sol} = 0.37\theta_{gel} \quad (3)$$

It should be noted that the time required for gelation at this gelation temperature was 5 min. Thus, this result indicates that the structuring in the gel phase proceeds very slowly. The structuring may represent both the increase of the number of cross-links and the growth of them. Since the diffusion rate of water is lower in the well-grown polymer-rich regions containing these cross-links than in the solution, t_{sol} is larger than the induction time for gelation. For a given polymer concentration, t_{sol} must be a function of the temperature differences between T_{gel} and T_t and T_{sol} and T_t and the storing time θ_{gel}. We will in the next work measure t_{sol} in various conditions to functionalize it in detail.

Conclusions

For the following five reasons, the polymer which shows LTS-type sol–gel transition could be synthesized by the substitution of the chlorine atoms of poly(dichlorophosphazene). (1) Each phosphorus atom in the main chain had two reactive P–Cl bonds. Because of this, the fine molecular design was possible. (2) In the first stage of the substitution, there were very few cases where two chlorines bonded to the same phosphorus atom were together replaced by ethylamino and/or ethoxy groups under the mild reaction condition used here. (3) In the second stage of the substitution, the remaining chlorine atoms were clearly replaced by the hydroxyl groups, for the high hydrolytic sensitivity of the P–Cl bonds. Subsequently, on the monomeric unit where both chlorines were replaced with the hydroxyl groups, cleavage of the main chain occurred. (4) The hydroxyl groups could form hydrogen bonds with the other groups to cause gelation. (5) The polymeric nature could be left in the product, in spite of the partial hydrolysis of the main chain. By conditions 1, 2, and 3, the finely balanced structure was yielded. Further, the polymer could have low-temperature solubility in water and cause the high-temperature phase separation. By conditions 4 and 5, the gelation could be caused in the two-phase region.

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References and Notes

(1) Tanigami, T.; Suzuki, H.; Yamaura, K.; Matsuzawa, S. *Macromolecules* **1985**, *18*, 2595. Tanigami, T.; En, K.; Yamaura, K.; Matsuzawa, S. *Polym. J.* **1986**, *18*, 31.
(2) Tan, M. H.; Moet, A.; Hiltner, A.; Baer, E. *Macromolecules* **1983**, *16*, 28.
(3) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.
(4) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709.
(5) Allcock, H. R.; Kugel, R. L. *Inorg. Chem.* **1966**, *5*, 1716.
(6) Allcock, H. R. *Phosphorus Nitrogen Compounds*; Academic: New York, 1972.
(7) Allcock, H. R.; Austin, P. E.; Neenan, T. X. *Macromolecules* **1982**, *15*, 689.
(8) Allcock, H. R.; Neenan, T. X.; Kossa, W. C.; *Macromolecules* **1982**, *15*, 693.
(9) Allcock, H. R. *Chem. Eng. News* **1985**, *March 18*, 22.
(10) Allcock, H. R.; Connolly, M. S. *Macromolecules* **1985**, *18*, 1330.
(11) Allcock, H. R.; Lavin, K. D.; Riding, G. H. *Macromolecules* **1985**, *18*, 1340.
(12) Allcock, H. R.; Neenan, T. X. *Macromolecules* **1986**, *19*, 1495.
(13) Allcock, H. R.; Kwon, S. *Macromolecules* **1986**, *19*, 1502.
(14) Allcock, H. R.; Austin, P. E.; Neenan, T. X.; Sisko, J. T.; Blonsky, P. M.; Shriver, D. F. *Macromolecules* **1986**, *19*, 1508.
(15) Allcock, H. R.; Riding, G. H.; Lavin, K. D. *Macromolecules* **1987**, *20*, 6.
(16) Kim, C.; Allcock, H. R. *Macromolecules* **1987**, *20*, 1727.
(17) Allcock, H. R.; Mang, M. N.; McDonnell, G. S.; Parvez, M. *Macromolecules* **1987**, *20*, 2060.
(18) Allcock, H. R.; Brennan, D. J.; Graaskamp, J. M. *Macromolecules* **1988**, *21*, 1.
(19) Allcock, H. R.; Connolly, M. S.; Sisko, J. T.; Al-Shali, S. *Macromolecules* **1988**, *21*, 323.
(20) Singler, R. E.; Schneider, N. S.; Hagnauer, G. L. *Polym. Eng. Sci.* **1975**, *15*, 321.
(21) Wisian-Neilson, P.; Ford, R. R.; Neilson, R. H.; Roy, A. K. *Macromolecules* **1986**, *19*, 2091.
(22) Ferrar, W. T.; Marshall, A. S.; Whitefield, J. *Macromolecules* **1987**, *20*, 317.
(23) Gleria, M.; Bolognesi, A.; Porzio, W.; Catellani, M.; Destri, S.; Audisio, G. *Macromolecules* **1987**, *20*, 469.
(24) Neilson, R. H.; Hani, R.; Wisian-Neilson, P.; Meister, J. J.; Roy, A. K.; Hagnauer, G. L. *Macromolecules* **1987**, *20*, 910.
(25) Tanigami, T.; Ohta, H.; Yamaura, K.; Matsuzawa, S., unpublished work.
(26) Kunieda, H.; Shinoda, K. In *Colloidal Dispersions and Micellar Behavior*; Mittal, K. L., Ed.; ACS Symposium Series; American Chemical Society: Washington, DC, 1975; p 278.
(27) Eldridge, J. E.; Ferry, J. D. *J. Phys. Chem.* **1954**, *58*, 992.