Macromolecules 1991, *24*, 2719–2724

Stereocomplex Formation between Enantiomeric Poly(lactic acid)s. 2. Stereocomplex Formation in Concentrated Solutions

Hideto Tsuji,[†,§] Fumitaka Horii,[†] Suong-Hyu Hyon,[‡] and Yoshito Ikada[*,‡]

Research Center for Biomedical Engineering, Kyoto University, 53 Kawahara-cho, Shogoin, Sakyo-ku, Kyoto 606, Japan, and Institute for Chemical Research, Kyoto University, Uji City, Kyoto 611, Japan

Received September 6, 1990; Revised Manuscript Received November 29, 1990

ABSTRACT: An irreversible gel is formed through stereocomplexation, when a concentrated chloroform solution of poly(D-lactic acid) is mixed with that of poly(L-lactic acid). This complex formation was studied by viscometry and NMR spectroscopy. It was found that the polymer complex is more rapidly formed at a polymer mixing ratio close to 1/1 and at higher polymer concentrations. The phase diagram of gelation was determined at the equimolar mixing ratio. The radius of the polymer coil, calculated under the assumption that these coils just overlap at the gel point, is smaller than the hydrodynamic radius calculated from the intrinsic viscosity. NMR results show that the mobility of poly(lactic acid) chains hardly changes during gelation but gradually decreases over a long period of time such as 1 month. The insignificant reduction of the polymer chain mobility at the gel point suggests that a very small fraction of segments is sufficient to set the polymer solution to a gel. A DSC study suggests the cross-links to be composed of complexed microcrystallites.

Introduction

It is well-known that D- and L-forms of low molecular weight compounds can produce racemic crystals upon mixing if their molecular affinity is sufficiently strong. Some polymers are also known to form racemates composed of optically active D- and L-polymers,[1–10] which are generally called stereocomplexes.

D- and L-lactides, which are the cyclic monomers of poly(D-lactic acid) (PDLA) and poly(L-lactic acid) (PLLA), respectively, possess a melting point at 97.5 °C. In contrast, their racemic compound melts at 124 °C, a higher temperature than the melting point of D-lactide and L-lactide. We have already reported that PDLA and PLLA can form a stereocomplex with a melting point of 230 °C,[11] which is considerably higher than 180 °C, the melting temperature of PDLA and PLLA.[12] Similar phenomena have also been found for other polymers.[2–4]

An X-ray diffraction study on the stereocomplex from PDLA and PLLA revealed that its crystalline structure was different from that of the homopolymer.[11] When the optically active PDLA and PLLA were mixed together at the equimolar ratio, the resulting polymer complex was optically inactive due to optical compensation between PDLA and PLLA. PDLA and PLLA are crystalline polymers, and there should be optical compensation in the crystalline region as a whole. Tadokoro et al. pointed out that the optical compensations in optically inactive materials from optically active polymer constituents involve either (a) compensation in the unit cell, i.e., a racemic lattice, (b) compensation in the crystallite, or (c) intercrystallite compensation.[1] We have confirmed by a wide-angle X-ray scattering (WAXS) analysis that the crystallite of the poly(lactic acid) (PLA) stereocomplex takes the compensation type of a, forming a so-called racemic crystallite.[13,14] In the unit cell of PLA stereocomplex, PDLA and PLLA chains are packed side by side with a D-monomer unit to L-monomer unit ratio of 1/1.[13,14] Also, poly(*tert*-butylethylene oxide)[1] and poly(*tert*-butylethylene sulfide)[3] are reported to belong to type a. These two polymers were obtained as a mixture of *S*- and *R*-isotactic polymers by polymerization of the optically inactive monomers.

S- and *R*-forms of poly(α-methyl-α-ethyl-β-propiolactone),[4] poly[β-(1,1-dichloropropyl)-β-propiolactone],[10] poly(γ-benzyl glutamate),[5–8] and poly(methylbenzyl methacrylate)[9] have been reported to be able to form a stereocomplex. In these cases, their *S*- and *R*-monomers are separately polymerized, and the resulting polymers are physically blended. Stereocomplexes differ in melting point and WAXS pattern from their respective isotactic homopolymers.

Complex formation for isotactic (it) and syndiotactic (st) poly(methyl methacrylate) (PMMA) is most widely known among the polymeric stereocomplexes and has intensively been investigated using various techniques.[15–25] It has been found that when it- and st-PMMA form a stereocomplex in dilute solution with a strongly complexing solvent, the solution viscosity decreases, while in a concentrated solution of complexing solvent, an increase in viscosity is observed accompanying gelation.[15]

In a previous paper, we reported that a stereocomplex is formed when a ternary dilute chloroform solution of PDLA and PLLA is poured into methanol, although no change in viscosity of the dilute chloroform solution could be detected.[11] Therefore, the complex seems to form not in the dilute solution but during the precipitating process. At higher concentrations, however, we observed an increase in viscosity upon mixing, resulting in a phase change from sol to gel. In this paper, we describe the gelation due to PLA stereocomplex formation in the concentrated region, mostly using viscometry and ^{1}H NMR spectroscopy.

Experimental Section

Materials. PDLA and PLLA were synthesized with the method previously reported.[26] Methyl D-lactate with an optical purity of 97% was supplied by Daicel Chemical Industries, Ltd., Japan, and hydrolyzed to D-lactic acid. L-Lactic acid with an optical purity of 98% was purchased as a 90 wt % aqueous solution from CCA Biochem bv, The Netherlands. The oligomeric PLA's prepared by condensation polymerization of the free acids were thermally decomposed to yield the lactide monomers. Ring-opening polymerization was performed for each lactide in bulk at

---

[*] To whom correspondence should be addressed.

[†] Institute for Chemical Research.

[‡] Research Center for Biomedical Engineering.

[§] Present address: Technology Development Center, Toyohashi University of Technology, Tempaku-cho, Toyahashi 441, Japan.

0024-9297/91/2224-2719$02.50/0

Table I
Polymerization Conditions and Characteristics of the Resulting Polymers

	polymzn condition	polymer		
code no.	lauryl alcohol, wt %	$[\eta]$, dL/g	$\bar{M}_v$	$[\alpha]^{25}{}_D$, deg
D1	5.0	0.20	3.3×10^3	+143
D2	2.0	0.61	1.5×10^4	+155
D3	0.4	1.36	4.5×10^4	+155
L1	3.0	0.20	3.3×10^3	−146
L2	1.0	0.56	1.3×10^4	−153
L3	0.5	1.30	4.2×10^4	−154

140 °C for 10 h using stannous octoate (0.03 wt %) and lauryl alcohol as catalyst and initiator, respectively.[12] The polymerization conditions were the same for D- and L-lactides, and the resulting polymers were purified by the reprecipitation method using methylene chloride as solvent and methanol as precipitant.

The viscosity-average molecular weight ($\bar{M}_v$) of the polymers was determined from their intrinsic solution viscosity, $[\eta]$, in chloroform at 25 °C using the equation[27]

$$[\eta] = 5.45 \times 10^{-4} \bar{M}_v^{\,0.73} \tag{1}$$

The specific optical rotation, $[\alpha]$, of the polymers was measured in chloroform at a concentration of 1 g/dL at 25 °C using a Perkin-Elmer polarimeter 241 at a wavelength of 589 nm. The characteristics of the polymers used in this work are listed in Table I, together with the polymerization conditions. $[\alpha]^{25}{}_D$ values were approximately +150° for PDLA and −150° for PLLA, in good agreement with the literature values.[28]

Measurements. The solution viscosity of mixtures of PDLA and PLLA in chloroform was measured in a range of total polymer concentration from 7.5 to 17.5 g/dL at 25 °C using an Ostwald-type viscometer.

The sol–gel transition point of the mixed solutions was determined with two different methods: the test tube tilting method and the viscosity method. In the tilting method, a test tube was sealed after the addition of the solution and then totally immersed in a water bath kept at a constant temperature in a range from 0 to 50 °C. The temperature of the water bath was changed by using an electric heater. The test tube was occasionally tilted to examine whether or not the polymer solution was still fluid. The temperature below which tilting the test tube caused no flow was defined as the gel point of the solution. In the viscosity method, the gelation time was defined as the time when the solution viscosity approached an unmeasurably high value. The tube tilting method also allowed us to determine the gelation time.

^{1}H NMR (400-MHz) spectra for mixed solutions of PDLA and PLLA as well as a PDLA solution in deuteriated chloroform were measured on a Jeol JNM-GX400 NMR spectrometer with a total polymer concentration range from 12.5 to 17.5 g/dL at 25 °C. The deuteriation ratio of chloroform was 99%, and non-deuteriated chloroform was present. NMR tubes were sealed after the addition of the mixed solution and immersed in a water bath kept at 25 °C before the NMR measurement.

Melting temperatures and the enthalpies of fusion were measured by a Shimadzu DT-30B differential scanning calorimeter (DSC). Heating was performed under a flow of nitrogen gas at a rate of 10 °C/min. The temperature and the enthalpy of fusion was calibrated by using tin as a standard.

Results and Discussion

Figure 1 shows the relative viscosity of solutions of PDLA and PLLA at 25 °C, the initial viscosity being set to unity. D3 and L3 were used in this experiment since they give the polymer pair with the highest molecular weight, about 4×10^4. The polymer concentration was fixed at 15.0 g/dL. The polymer ratio in these experiments is expressed by the PDLA content in solution, X_D.

$$X_D = \mathrm{PDLA}/(\mathrm{PDLA} + \mathrm{PLLA}) \tag{2}$$

Thus, X_D equals 0.5 for an equimolar mixture. For solutions with X_D values of 0.5, 0.6, and 0.7, a viscosity rise is observed after short induction periods, followed by gelation. The reciprocal of the induction time (t_i) for the viscosity rise is plotted against X_D in Figure 2. As seen, the induction period becomes longer as X_D deviates from 0.5. A previous DSC study also showed that the most favorable X_D for the formation of PLA stereocomplex is 0.5.[11] For this reason, we kept X_D equal to 0.5 in the following experiments.

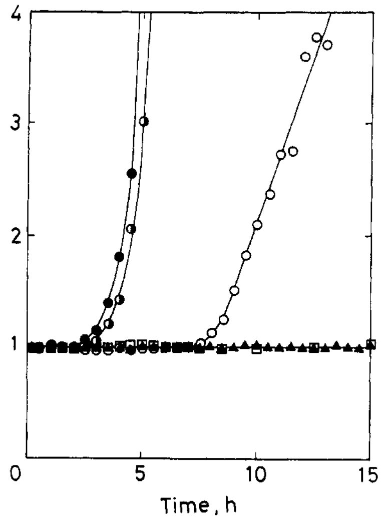

Figure 1. Relative viscosity (η_r) of solutions of D3 and L3 as a function of standing time at different X_D (15.0 g/dL, 25 °C). ●: 0.5, ◑: 0.6, ○: 0.7, ▲: 0.8, □: 1.

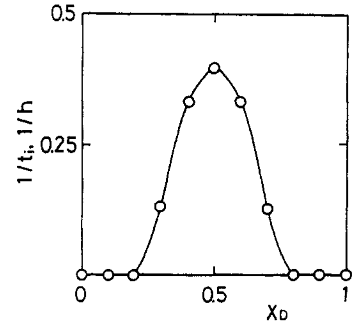

Figure 2. Reciprocal of time before a viscosity rise can be observed ($1/t_i$) for solutions of D3 and L3 at different X_D (15.0 g/dL, 25 °C).

Figure 3 shows the viscosity of solutions made from D3 and L3 at different polymer concentrations and 25 °C as a function of standing time. An appreciable viscosity rise is observed at polymer concentrations higher than 12.5 g/dL. The $1/t_i$ value where the viscosity rise is observed is plotted as a function of the total polymer concentration in Figure 4. The induction period becomes shorter with an increase in polymer concentration. The lowest concentration for gelation was approximately 10 g/dL for the D3–L3 pair at 25 °C. Such a significant dependence of the gelation point on the polymer concentration must be a reflection of polymer–polymer interactions necessary for gelation.

The sol–gel transition temperature of PDLA/PLLA solutions was determined by the tube tilting method. The sol–gel transition curve obtained for mixtures of D3 and L3 in chloroform at various concentrations is shown in Figure 5, together with the cloud-point curve. The curves divide the phase diagram into three regions, labeled I–III, as shown in Figure 5. In region I, the solution is always in a transparent and homogeneous sol state, while microgels of stereocomplex are formed in region II, causing the solution to appear cloudy. In region III, gelation occurs

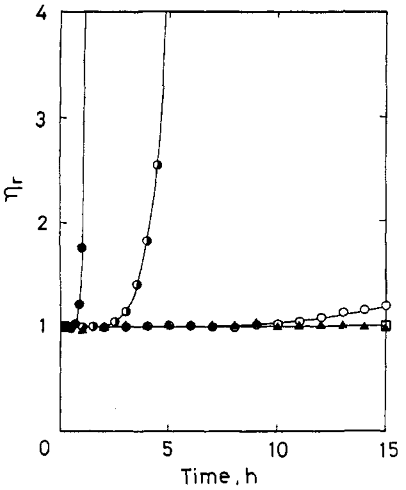

Figure 3. Relative viscosity (η_r) of solutions of D3 and L3 as a function of standing time at different polymer concentrations (25 °C, $X_D = 0.5$). □: 7.5 g/dL, ▲: 10.0 g/dL, ○: 12.5 g/dL, ◑: 15.0 g/dL, ●: 17.5 g/dL.

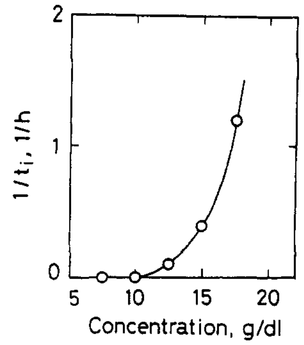

Figure 4. Reciprocal of time before a viscosity rise can be observed ($1/t_i$) for solutions of D3 and L3 at different polymer concentrations (X_D = 0.5, 25 °C).

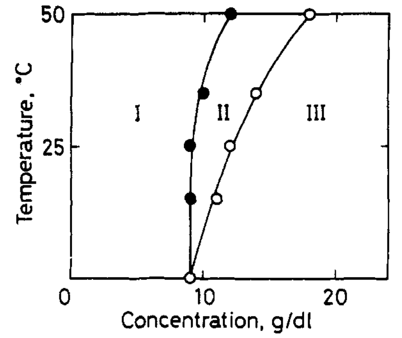

Figure 5. Phase diagram of the PDLA/PLLA/chloroform system (D3 + L3, X_D = 0.5).

Table II
Gelation Time Determined with the Tilting Tube Method (t_{gs}) and the Viscometry Method (t_{gv}) at 25 °C and Various Concentrations of Polymer

polym concn, g/dL	t_{gs}, h	t_{gv}, h
12.5	13	>15
15.0	1.5	5
17.5	0.8	1.3

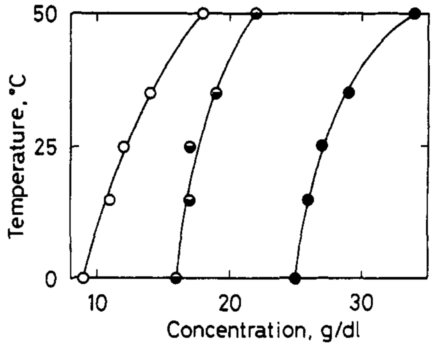

Figure 6. Gelation temperature of solutions of PDLA and PLLA of different molecular weights (X_D = 0.5, 25 °C). ●: D1 + L1, ◑: D2 + L2, ○: D3 + L3.

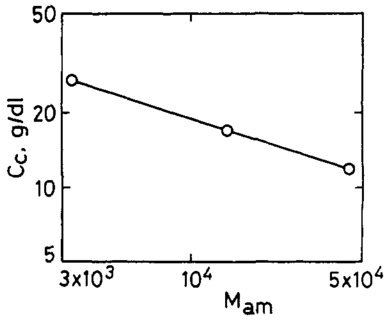

Figure 7. Relation between critical concentration for gelation (C_c) and the arithmetic mean of $\bar{M}_v$(PDLA) and $\bar{M}_v$(PLLA) (M_{am}) (X_D = 0.5, 25 °C).

macroscopically throughout the solution. Once the gels are formed, they cannot form a homogeneous solution any more even by raising the solution temperature or by diluting the solution with the solvent, indicating that the gelation process is irreversible. This property is different from that of the PMMA stereocomplex gel, which is thermoreversible,[15,16] suggesting stronger interaction between PDLA and PLLA molecules at cross-links than that between it- and st-PMMA molecules in associated parts.

The gelation time determined with the tube tilting method (t_{gs}) under quasi-static conditions and that obtained by viscometry (t_{gv}) under dynamic conditions are summarized in Table II. As can be seen, t_{gv} is much longer than t_{gs} for any polymer concentration. This delay may be caused by the destruction of the weakly formed ordered structure or by the suppression of formation of the ordered structure during the viscosity measurement, which puts the polymer solution in a dynamic flow state.

Figure 6 gives the transition temperature from sol to macroscopic gel for polymer pairs of three different molecular weights (D1 + L1, D2 + L2, and D3 + L3). As is apparent, the gelation curve shifts to higher concentrations as the molecular weight decreases. This behavior implies that the formation of a macroscopic gel requires direct contact between the PDLA and PLLA chains. It is disturbed by the solution flow but is stabilized by extensive interactions between the PDLA and PLLA chains. The critical concentration (C_c), below which the three-dimensional gel cannot be formed at 25 °C, is plotted as a function of the arithmetic mean [$\bar{M}_v$(PDLA) + $\bar{M}_v$(PLLA)]/2 (=M_{am}) in Figure 7. The linear relation found in Figure 7 can be given by

$$C_c M_{am}^{0.31} = 3.3 \times 10^2 \tag{3}$$

The shift of C_c to higher concentrations with a rise in temperature may be explained in terms of the chain mobility, which increases with the temperature rise, thus hindering the formation of the ordered structure.

If the polymer molecule can be represented by a swollen impervious particle, the volume available per particle in solution at the gel point is given by $100M/NC_c$, where M is the molecular weight of the polymer, N is Avogadro's number, and C_c is the critical concentration expressed in grams per deciliter.[29,30] Then, the radius of swollen particles (R_c) just contacting with each other can be given

Table III
Critical Concentration for Gelation (C_c), Calculated Polymer Coil Dimension (R_c), and Radius of Hydrodynamic Volume (R_e) at 25 °C

mixture	C_c, g/dL	R_c, Å	R_e, Å
D1 + L1	27	15	22
D2 + L2	17	29	50
D3 + L3	12	48	98

by the equation

$$4\pi R_c^3/3 \times 1/0.74 = 100M/NC_c \tag{4}$$

where 0.74 is the volume fraction of swollen particles in a closed-packing array. On the other hand, $[\eta]$ may be related to the effective hydrodynamic volume of the polymer (R_e) through the equation

$$[\eta] = 0.025(4\pi/3)(R_e^3N/M) \tag{5}$$

where 0.025 is the coefficient of the Einstein equation for the viscosity of dispersions.[31] Combining eqs 1–5 gives

$$5.45 \times 10^{-4}\bar{M}_v^{0.73} = 0.025(4\pi/3)(R_e^3N/M) \tag{6}$$

Table III gives the R_c values calculated from eq 4 using C_c determined at 25 °C for polymer parts of various molecular weights under the assumption that the polymer coils just overlap at C_c. The R_e values calculated from eq 6 are also given in Table III. In the calculation of R_c and R_e, it was assumed that the arithmetic mean, M_{am}, is equal to M and $\bar{M}_v$. As seen in Table III, R_c is smaller than R_e. Provided the above simplified assumptions are correct, this finding implies that the gelation of mixed solutions through complex formation takes place at a higher polymer concentration than the overlapping concentration. This is different from the gelation of polymer solution through radiation cross-linking,[29,30] in which R_c was larger than R_e and region I was not observed. In other words, microgels were formed at any concentration below C_c. It seems reasonable that a certain amount of overlapping of chains is necessary for gelation through complex formation, because gelation is due to physical cross-linking, which generally requires extensive polymer–polymer interactions.

To give an insight on the mobility of the PLA chain in the course of gelation, ^{1}H NMR measurements were performed in region III after mixing the PDLA and PLLA solutions. For these measurements, D3 and L3 were used at a mixing ratio of 0.5. As is well-known from the NMR theory,[32] the resonance lines that are observed at a frequency ν_0 can cause transition between neighboring levels of high-mobility molecules. ν_0 is given by

$$\nu_0 = \gamma H_0/2\pi \text{ (Hz)} \tag{7}$$

where γ is the gyromagnetic ratio and H_0 is the static field. Figure 8 gives the NMR spectra of the CH and CH_3 groups of PLA molecules and of the solvent at different standing times. The polymer concentration is 17.5 g/dL. For the CH and CH_3 groups, resonance lines with somewhat broader shoulders appear after 6 h, indicating the restricted mobility of the PLA segments. Since the apparent gelation comes to completion in about 50 min (t_{gs}) at this concentration, these broad shoulders appearing at 6 h may be assigned to segments connecting cross-linked regions that are probably composed of complexed microcrystallites. It appears that the segments in the complexed crystallite show no NMR spectrum because of their entirely frozen mobility. The effect of segment-connecting cross-links could not be observed on the NMR spectra, probably because of a small amount and a small size of the complexed crystallites even at short times. The shoulders seem to become broader, shifting downfield, as the complexed microcrystallites gradually grow with time. In other words, the slow long-term changes in the NMR spectra indicate that the growth rate of complexed crystallites functioning as cross-links is extremely low. Sharp lines, identical with those of the homopolymers, are observed even after gelation, suggesting the existence of freely movable PLA segments in the gel. The spectra of the homopolymer solution remained unchanged for 27 days.

The resonance line of $CHCl_3$ exhibits a change with time similar to that of the CH and CH_3 groups of the polymers in contrast to pure $CHCl_3$, which showed only a single sharp line for 1 month. A shoulder appears at about 6 h and becomes gradually broader, shifting downfield. The $CHCl_3$ molecules giving rise to the broad shoulder may be assigned to those trapped in the PLA complexed crystallites, thereby having lower mobility.

NMR relative integrated intensity (I_r) of the CH and CH_3 groups can be calculated from the relation

$$I_r = I_t/I_0 \tag{8}$$

where I_0 and I_t are the integrated intensity of the resonance lines at times 0 and t, respectively. Since the PLA segments in the crystalline regions have very low mobility, they cannot give any resonance. Thus a reduction of I_r indicates an increase in the mass fraction of polymer in the crystalline region.

I_r for the CH line is plotted against the standing time in Figure 9. It is seen that the reduction of I_r at 1.5 h is insignificant even for the 17.5 g/dL solution, which undergoes gelation within 50 min. This suggests that only a small fraction of segments are sufficient to form microcrystallites as cross-links for macroscopic gelation. I_r at 17.5 g/dL gradually reduces to 0.47 in about 1 month, revealing that the stereocomplex crystalline region continues to increase long after gelation. The initial decrease of I_r increases with the solution concentration, meaning that the crystallization takes place more rapidly, at least in the initial stage, as the solution concentration becomes higher. The change of I_r with time for the CH_3 group was virtually the same as that observed with the CH group, suggesting that no group exhibits any particular interaction in the gel.

A DSC study was performed on a dried stereocomplex gel and a homopolymer film of D3. The dried gel used for the DSC measurement was obtained by the following procedure. A test tube containing an equimolar mixture of D3 and L3 polymers in chloroform was sealed and immersed in a water bath kept at 25 °C. After 1 month, the gel was washed with $CHCl_3$ to remove the PLA molecules, followed by drying in vacuo at 50 °C for 1 week to a constant weight. The dried gel gave only a single endothermic peak at about 216 °C, identical with the melting temperature (T_m) of the PLA stereocomplex.[12] It should be stressed that no peak was observed at 180 °C, which is the melting temperature of the homopolymer. If crystallites cannot form any more after drying but only during gelation in solution, then the cross-links that caused gelation of the solution must be composed of complex crystallites. The T_m of this complex is slightly lower than 230 °C, which was reported elsewhere,[11] and its enthalpy of fusion (ΔH_m) is 30 J/g of polymer, 2–3 times smaller than that of the complex film (84 J/g of polymer) prepared by casting a 1 g/dL chloroform solution of the D3 and L3 polymers at room temperature.

Spěváček and Schneider reported a ^{1}H NMR study on a PMMA complex gel formed at 10 g/dL.[18] All the resonance lines of the PMMA complex gel in benzene

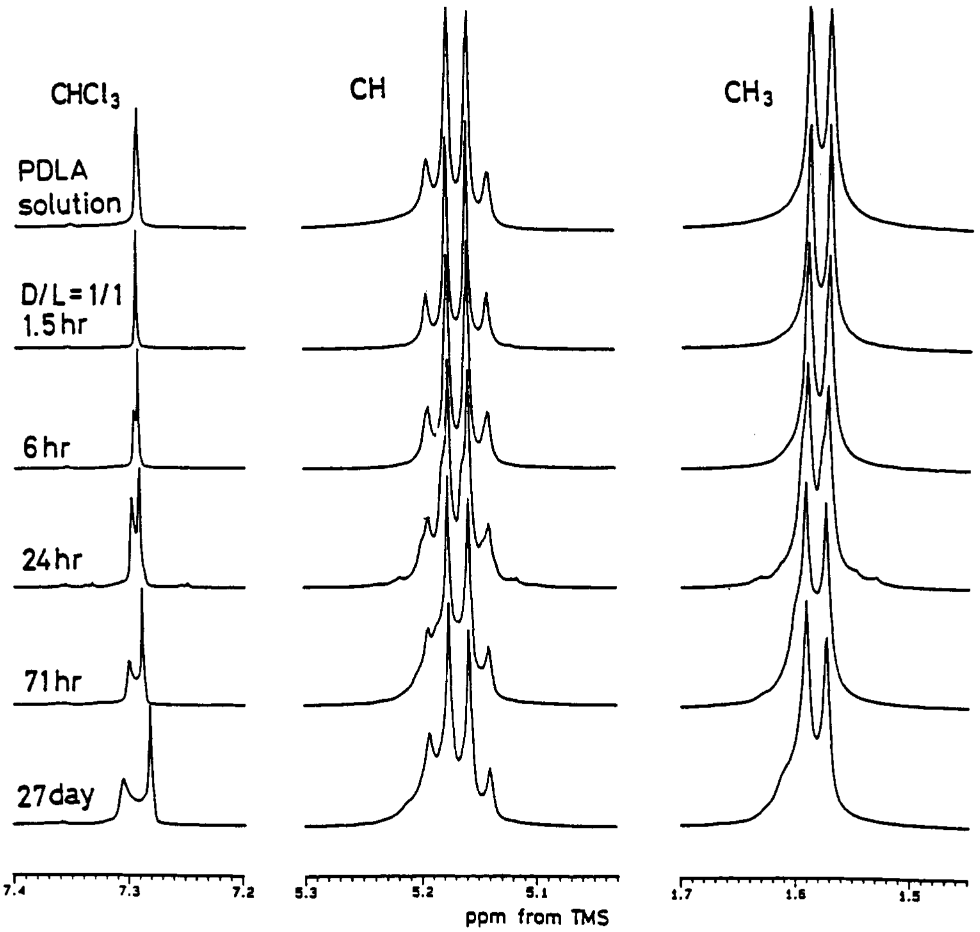

Figure 8. 400-MHz ^{1}H NMR spectra of solutions of D3 and L3 (X_D = 0.5) and a solution of D3 in chloroform-*d* (17.5 g/dL, 25 °C).

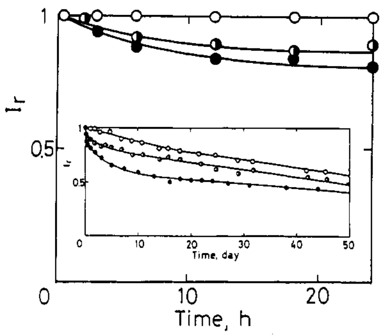

Figure 9. Relative NMR intensity (I_r) of the CH group of solutions of D3 and L3 as a function of standing time at different polymer concentrations (X_D = 0.5, 25 °C). ○: 12.5 g/dL, ◑: 15.0 g/dL, ●: 17.5 g/dL.

became broader, accompanying a decrease in the integrated intensity, similar to the result observed on our PLA complex gel in chloroform. However, some of the PMMA complex gels gave virtually no sharp resonance lines in benzene, acetonitrile, and carbon tetrachloride. This reveals that approximately all the PMMA molecules took part in complexation, in contrast to the PLA complex gel. To compare in more detail the difference in complexation between PLA and PMMA, further investigations by NMR spectroscopy are needed.

Conclusion

The above findings lead us to propose a model (Figure 10) for the gel structure formed from equimolar PDLA and PLLA mixtures in concentrated solutions of chloroform in region III. Crystallites of homopolymers, PDLA or PLLA, do not form in the concentrated chloroform solution, but a small amount of cross-links, or crystallites, is initially produced as a result of stereocomplexation. These crystallites induce an increase in solution viscosity and finally gel formation. The PLA complex gel is thermoirreversible in contrast to the thermoreversible PMMA complex gel, suggesting that there is a stronger interaction between PDLA and PLLA molecules in crystalline regions than that between it- and st-PMMA molecules in the associated state. From NMR measurements, the growth of crystallites appears to continue for a very long time in the gel phase of the solution.

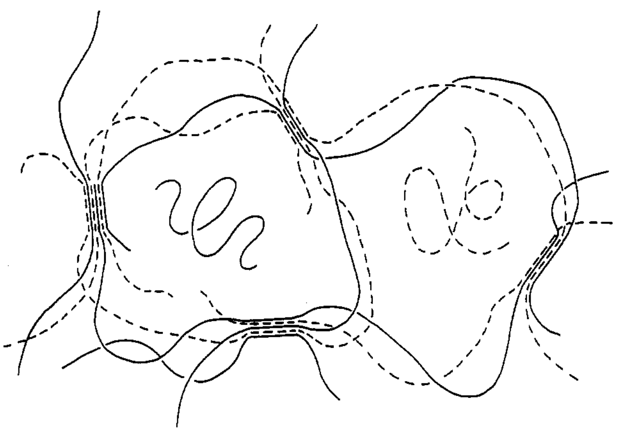

Figure 10. Structure model of the complex gel in region III: (—) PDLA; (- - -) PLLA.

Acknowledgment. Grateful acknowledgment is made to Mr. Minoru Inagaki (Institute for Chemical Research, Kyoto University) for optical rotation measurements.

References and Notes

(1) Sakakihara, H.; Takahashi, Y.; Tadokoro, H.; Oguni, N.; Tani, H. *Macromolecules* **1973**, *6*, 205.

(2) Dumas, P.; Spassky, N.; Sigwalt, P. *Makromol. Chem.* **1972**, *156*, 55.

(3) Matsubayashi, H.; Chatani, Y.; Tadokoro, H.; Dumas, P.; Spassky, N.; Sigwalt, P. *Macromolecules* **1977**, *10*, 996.

(4) Grenier, D.; Prud'homme, R. E. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 577.

(5) Baba, Y.; Kagemoto, A. *Macromolecules* **1977**, *10*, 458.

(6) Fukuzawa, T.; Uematsu, I.; Uematsu, Y. *Polym. J.* **1974**, *6*, 537.

(7) Yoshikawa, M.; Tsujita, Y.; Uematsu, I.; Uematsu, Y. *Polym. J.* **1975**, *7*, 96.

(8) Matsushima, N.; Hikichi, K.; Tsutsumi, A.; Kaneko, M. *Polym. J.* **1975**, *7*, 382.

(9) Hatada, K.; Shimizu, S.; Terawaki, Y.; Ohta, K.; Yuki, H. *Polym. J.* **1981**, *13*, 811.

(10) Voyer, R.; Prud'homme, R. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29*, 611.

(11) Ikada, Y.; Jamshidi, H.; Tsuji, H.; Hyon, S.-H. *Macromolecules* **1987**, *20*, 904. This is the first paper of this series.

(12) Hyon, S.-H.; Jamshidi, K.; Ikada, Y. In *Polymers as Biomaterials*; Shalaby, S. W., Hoffman, A. S., Ratner, B. D., Horbett, T. A., Eds.; Plenum Press: New York, London, 1984; pp 51–65.

(13) Okihara, T.; Tsuji, M.; Kawaguchi, A.; Katayama, K.; Tsuji, H.; Hyon, S.-H.; Ikada, Y., to be published in *J. Macromol. Sci.*

(14) Okihara, T.; Kawaguchi, A.; Tsuji, H.; Hyon, S.-H.; Ikada, Y.; Katayama, K. *Bull. Inst. Chem. Res. (Kyoto Univ.)* **1988**, *66*, 271.

(15) Watanabe, W. H.; Ryan, C. F.; Fleischer, P. C., Jr.; Garet, B. S. *J. Phys. Chem.* **1961**, *65*, 896.

(16) Ryan, C. F.; Fleischer, P. C., Jr. *J. Phys. Chem.* **1965**, *69*, 3384.

(17) Miyamoto, T.; Inagaki, H. *Macromolecules* **1969**, *2*, 554.

(18) Spěváček, J.; Schneider, B. *Makromol. Chem.* **1974**, *175*, 2939.

(19) Spěváček, J.; Schneider, B. *Makromol. Chem.* **1975**, *176*, 729.

(20) Challa, G.; De Boer, A.; Tan, Y. Y. *Int. J. Polym. Mater.* **1976**, *4*, 239.

(21) Vorenkamp, E. J.; Bosscher, F.; Challa, G. *Polymer* **1979**, *20*, 59.

(22) Konnecke, K.; Rehage, G. *Colloid Polym. Sci.* **1981**, *259*, 1062.

(23) Bosscher, F.; Brinke, G. T.; Challa, G. *Macromolecules* **1982**, *15*, 1442.

(24) Schomaker, E.; Challa, G. *Macromolecules* **1988**, *21*, 2195.

(25) Schomaker, E.; Hoppen, H.; Challa, G. *Macromolecules* **1988**, *21*, 2203.

(26) Sorenson, W. R., Campbell, T. W., Eds. *Preparative Methods of Polymer Chemistry*; Wiley: New York, 1961.

(27) Schindler, A.; Harper, D. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 2593.

(28) Tonelli, A. E.; Flory, P. J. *Macromolecules* **1969**, *2*, 225.

(29) Sakurada, I.; Ikada, Y. *Bull. Inst. Chem. Res. (Kyoto Univ.)* **1962**, *40*, 25.

(30) Sakurada, I.; Ikada, Y. *Bull. Inst. Chem. Res. (Kyoto Univ.)* **1964**, *42*, 22.

(31) Einstein, A. *Ann. Phys.* **1911**, *34*, 591.

(32) See, for example: Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. *High Resolution NMR Spectroscopy*; Pergamon: Oxford, 1965; Chapter 2.