Viscoelastic Properties of Stereocomplex Polymers

YUICHI MORI and HIROSHI TANZAWA, *Basic Research Laboratory Toray Industries, Inc., Kamakura, Kanagawa, Japan*

Synopsis

Stereocomplex polymers were synthesized by radical polymerization of mixtures of isotactic and syndiotactic poly(methyl methacrylate) (PMMA) in some vinyl monomers under the conditions of stereocomplex formation. The viscoelastic properties of stereocomplex polymers were studied by a sinusoidal vibration method and compared with those of the usual blended polymers. It was found that the network structure resulting from the stereocomplex association between isotactic and syndiotactic PMMA prevents a phase separation of the newly created polymers from the matrix of PMMA during the polymerization process, and that makes the viscoelastic properties and optical transparency of stereocomplex polymers very different from those of the usual blended polymers without stereocomplex formation.

INTRODUCTION

It is well known that the mixing of solutions of isotactic and syndiotactic PMMA in polar solvents, such as dimethylformamide and acetonitrile, instantly results in a gel which has a distinct melting temperature in thermally reversible change between gel and sol states.[1-4] By the techniques of viscometry, x-ray diffraction, high-resolution NMR, light scattering, ultracentrifugation, and thin-layer chromatography, the mechanism of the gelation has been studied.[5-14] It is proposed that the steric complementarity (stereocomplex) between isotactic and syndiotactic repeating sequences forms a network structure including the solvent.

The gelation was also observed by mixing solutions of these two tactic polymers in certain vinyl monomers. We obtained stereocomplex polymers by means of polymerizing the vinyl monomers in the gel containing these two tactic PMMA. The polymerization was carried out at a temperature lower than the melting temperature of the gel in order to preserve the gel state. These stereocomplex polymers are very different from the polymers prepared by the usual blend techniques in their mechanical, optical and thermal properties and in their durability for solvents. Thus, stereocomplex polymers are interesting from the industrial viewpoint.

The present paper reports specifically on the dynamic mechanical properties of these stereocomplex polymers.

EXPERIMENTAL

Preparation of Isotactic and Syndiotactic PMMA

Isotactic PMMA of low molecular weight (LI) was prepared by anionic polymerization of 250 ml methyl methacrylate (MMA) at −20°C in 500 ml tolu-

TABLE I
Values of Viscosity and Tacticity Parameters for Anionic and Radical PMMA

Polymer	$[\eta]$	I, %	H, %	S, %
HI	2.55	95	3	2
LI	0.58	90	7	3
LHS	6.20	9	42	49
LLS	0.40	9	42	49
HHS	3.35	0	28	72

ene containing 0.2% phenylmagnesium bromide. The mixture was stirred for 7 hr in nitrogen atmosphere.

Isotactic PMMA of high molecular weight (HI) was prepared by polymerization of 250 ml MMA at 0°C in 300 ml toluene containing 0.2% phenylmagnesium bromide. This was stirred for 3 hr in nitrogen atmosphere. Both polymers were precipitated using a mixture of methyl alcohol and hydrochloric acid (1:1). The precipitates were purified by redissolving in benzene and reprecipitating with petroleum ether.

Low-syndiotactic PMMA of low molecular weight (LLS) was prepared by suspension polymerization in water at 80°C, using azobisisobutyronitrile as an initiator and n-dodecylmercaptan as a chain transfer reagent.

Low-syndiotactic PMMA of high molecular weight (LHS) was prepared by bulk polymerization at 50°C, using azobisisobutyronitrile as an initiator.

High-syndiotactic PMMA of high molecular weight (HHS) was prepared by polymerizing 35 ml MMA in 280 ml dimethoxyethane containing 23 mg sodium naphthalene as a catalyzer. The mixture was stirred at −78°C for 6 hr in nitrogen atmosphere and was precipitated using a mixture of methyl alcohol and hydrochloric acid (1:1). These three polymers were purified by redissolving in acetone and reprecipitating with water.

The viscosities of the polymers were measured in chloroform solutions at 25°C. The microtacticity parameters of the polymers were also determined by 100-MHz NMR measurements.[15] The isotactic (I), heterotactic (H), syndiotactic triad (S), and the values of viscosity of the polymers are shown in Table I.

Sample Preparation

Stereocomplex polymers were prepared by the following procedure. The isotactic and syndiotactic PMMA (LI and LLS) were independently dissolved in MMA, methyl acrylate (MA), and ethyl acrylate (EA) monomers, respectively. One monomer solution of the isotactic PMMA (LI) and the corresponding monomer solution of the low-syndiotactic PMMA (LLS) were well mixed, adding 0.2% azobisisobutyronitrile to the sol above the melting temperature of the gel. Then the monomer solution mixture was poured into a glass cell composed of two sheets of glass and a sandwiched spacer suitable for casting a film, and was chilled below the melting temperature in order to change the sol into the gel. Then the monomers in the gel were photo-polymerized at 0°C for 15 hr, using a 450-watt high-pressure mercury lamp. Finally, the polymers were cured at 90°C for 6 hr.

TABLE II
Chemical Composition of Stereocomplex Polymers, Blended Polymers,
and Copolymer before Polymerization

Sample name	PMMA com-position, wt-%	Ratio[a]	Monomer	Monomer com-position, wt-%
S-MMA	20	0.0	MMA	80
IS-MMA	20	0.5	MMA	80
I-MMA-1	10	Iso.	MMA	90
I-MMA-2	20	Iso.	MMA	80
S-EA	20	0.0	EA	80
IS-EA-1	20	0.2	EA	80
IS-EA-2	20	0.5	EA	80
IS-EA-3	20	1.0	EA	80
IS-EA-4	20	2.0	EA	80
IS-EA-5	20	5.0	EA	80
I-EA	20	Iso.	EA	80
MMA-EA	—	—	MMA, EA	20, 80
S-MA	20	0.0	MA	80
IS-MA-1	20	0.2	MA	80
IS-MA-2	20	0.5	MA	80
IS-MA-3	20	2.0	MA	80
IS-MA-4	20	5.0	MA	80
I-MA	20	Iso.	MA	80

[a] Ratio of isotactic to syndiotactic PMMA.

Blended polymers were prepared by polymerizing independently the mo-
nomer solutions of the isotactic PMMA (LI) and the low-syndiotactic PMMA
(LLS) in MMA, MA, and EA monomers under the above-mentioned condi-
tions, without mixing the monomer solutions of the isotactic and syndiotactic
PMMA.

Copolymers were also prepared by photo-induced polymerization of the
mixtures of MMA and MA monomers and of MMA and EA monomers, re-
spectively, under the same conditions as stereocomplex polymers and the
blended polymers were prepared. The chemical compositions of the poly-
mers prepared are shown in Table II.

Measurement of Melting Temperatures of Gels

The solutions of isotactic and syndiotactic PMMA in a variety of vinyl mo-
nomers containing hydroquinone as an inhibitor of polymerization were
mixed well in glassy test tubes and kept for a day at room temperature in
order to complete the gelation. Melting temperature was defined as the tem-
perature at which flow began in the gel within a test tube undergoing rotation
in the vertical plane. The whole apparatus was in a water bath with a con-
stant rate of increase in temperature of 1°C/2 min.

Measurement of Dynamic Mechanical Properties

The variations with temperature of the dynamic modulus (E'), the dynam-
ic loss modulus (E''), and the loss tangent (tan δ) of the samples were mea-
sured by sinusoidal vibration method, using a direct-reading Dynamic Vis-
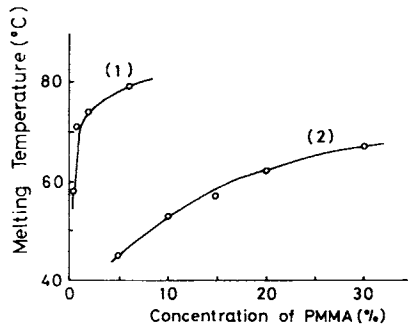
Fig. 1. Total polymer concentration dependence of the melting temperature of the gel of MMA monomer at a constant ratio of isotactic to syndiotactic PMMA (0.2): (1) HI-LHS; (2) LI-LLS.

coelastometer, Vibron Model DD-II made by Toyosokki Co. The measurements were carried out at approximately 5°C intervals between −60°C and 140°C at a fixed frequency, 110 Hz. The sample sizes varied from species to species within the ranges of 1.0 to 2.0 cm in length, 0.3 to 0.5 cm in width, and 50 to 200 μ in thickness.

RESULTS AND DISCUSSION

Melting Temperature

It is suggested that melting temperature of the gel formed by mixing solutions of isotactic and syndiotactic PMMA can be regarded as the temperature of the dissociation of the stereocomplex and, consequently, as a measure of steric interaction force between isotactic add syndiotactic sequences of PMMA. In order to determine the synthesizing conditions of stereocomplex polymers, the melting temperatures of the gels, comprising a variety of vinyl monomers, were measured as functions of the molecular weight, the composition, the total concentration, and the tacticity of the constituent polymers. Figures 1 and 2 show the variations of the melting temperatures of the gels of MMA monomer with the total concentration of PMMA at a constant ratio of
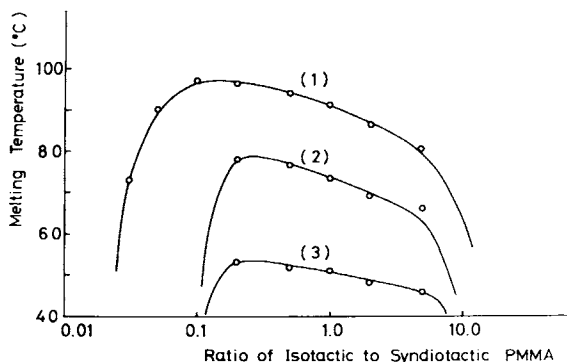

Fig. 2. Relation between the ratio of isotactic to syndiotactic PMMA and the melting temperature of the gel of MMA monomer at a constant total polymer concentration (C): (1) HI-HHS (C = 5%); (2) HI-LHS (C = 5%); (3) LI-LLS (C = 10%).

isotactic to syndiotactic PMMA (0.2) and with the ratio of isotactic to syndiotactic PMMA at a fixed total polymer concentration, respectively.

As indicated in Figure 1, melting temperature increases with total polymer concentration and with the molecular weight of two tactic PMMA. In the gels from low molecular weight tactic PMMA (LI-LLS) and from high molecular weight tactic PMMA (HI-LHS), the stereocomplex association is formed stoichiometrically in the ratio (0.2) where the maxima of melting temperature are located (Fig. 2). In the gel from high molecular weight isotactic (HI) and high-syndiotactic PMMA (HHS) instead of low-syndiotactic PMMA (LHS), the melting temperature is maximum at a ratio of about 0.1, and gel state is not formed at room temperature at a ratio of less than 0.02 and more than 20.0. The range of the ratio of isotactic to syndiotactic PMMA for gelation seems to be independent of the molecular weight of the two tactic PMMA's but to depend upon the tacticity of the constituent PMMA. Further, although the molecular weight of HSS is less than that of LHS, the melting temperature of the gel (HI-HHS) is much higher than that of the gel (HI-LHS) over the entire ratio range. This suggests that tacticity plays the most important role in the gelation process.

From these studies on the melting temperature of the gel, polymerization temperature, ratio of isotactic to syndiotactic PMMA, and polymer concentration of gel were determined.

Dynamic Viscoelasticity of Stereocomplex Polymers of Methyl Methacrylate

Temperature dependence of loss tangent (tan δ) for stereocomplex polymer (IS-MMA) and for blended polymers (S-MMA, I-MMA-1, and I-MMA-2) is shown in Figure 3. Since radical polymerization of MMA monomer gives a syndiotactic PMMA, blended polymer (S-MMA), which was prepared by radical polymerization of MMA monomer solution of syndiotactic PMMA (LLS), is a syndiotactic PMMA. In blended polymer (S-MMA), rapid increase in tan δ at about 110°C is caused by micro-Brownian motion of syndiotactic polymer main chains (α-process),[16] and the maximum of tan δ in the vicinity of 50°C results from the motion of the ester side chains of PMMA (β-process).[17]

In stereocomplex polymer (IS-MMA) and blended polymers (I-MMA-1 and I-MMA-2), temperature dependence of tan δ is very similar. The temperature of α-process for IS-MMA, I-MMA-1, and I-MMA-2 is higher than that for S-MMA by 5° to 10°C. In IS-MMA, I-MMA-1, and I-MMA-2, the loss peak observed in the vicinity of 50°C in S-MMA disappears, and another new loss peak appears in the range of 80°C to 90°C. The values of the apparent activation energy for these new loss peaks range from 18 to 26 Kcal/mole, and these values are approximately equal to the literature values of the activation energy of β-process of syndiotactic PMMA (S-MMA).[17] Therefore, it is thought that the β-process of PMMA in IS-MMA, I-MMA-1, and I-MMA-2 shifts to a temperature range higher by 30° to 40°C than that of the β-process of PMMA in S-MMA.

The close similarity in temperature dependence of tan δ between stereocomplex polymer (IS-MMA) and blended polymers (I-MMA-1 and I-MMA-
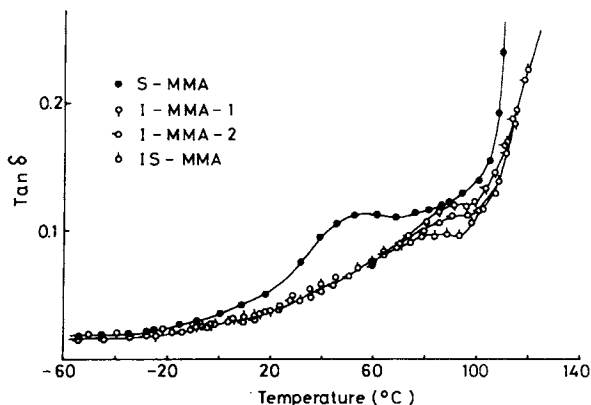
Fig. 3. Temperature dependence of tan δ for stereocomplex polymer and the blended polymers of MMA monomer.

2) suggests that even in blended polymers (I-MMA-1 and I-MMA-2) the stereocomplex association can be formed between the isotactic PMMA dissolved in MMA monomer and the syndiotactic PMMA newly created by radical polymerization of MMA monomer during the polymerization process. There is no substantial difference in the dynamic mechanical properties between stereocomplex polymer (IS-MMA) which was polymerized after completing the stereocomplex association in MMA monomer solutions and blended polymers (I-MMA-1 and I-MMA-2) which were polymerized simultaneously with stereocomplex formation.

The shift of the β-process to higher temperature range in IS-MMA, I-MMA-1, and I-MMA-2 suggests that the stereocomplex association restricts especially the motion of the ester side chains of two tactic PMMA's. The ester side-chain interaction between isotactic and syndiotactic PMMA contributes significantly to the stereocomplex association. The study of the high-resolution NMR peaks of the ester methyl protons of isotactic and syndiotactic PMMA also suggests that even in gel state the stereocomplex association restrains the motions of the ester side chains of two tactic PMMA's.[8]
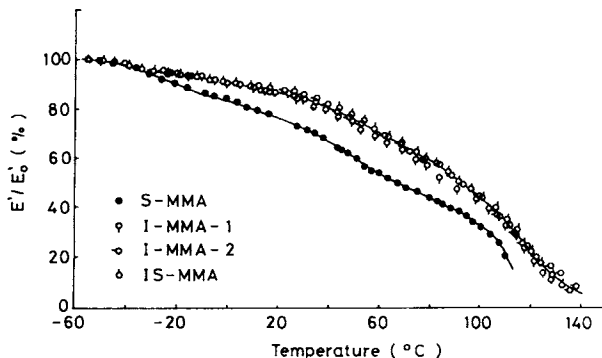

Fig. 4. Temperature dependence of the dynamic modulus of stereocomplex polymer and the blended polymers of MMA monomer.

In a blended polymer of isotactic PMMA and syndiotactic PMMA without stereocomplex formation, α-process of the blended polymer would occur at a temperature between about 50°C of α-process of isotactic PMMA[18] and about 100°C of α-process of syndiotactic PMMA. However, in stereocomplex polymers, α-process occurs at a temperature higher than 110°C. This means that a mutual interlocking of the side chains of isotactic and syndiotactic PMMA also restricts the motion of the main chains of the two tactic PMMA's.

Figure 4 shows the ratio of dynamic modulus to that at $-60°C$ (E'/E_0') as a function of temperature. Here it is also found that the restriction of the motion of main chains and side chains of the two tactic PMMA by the stereocomplex association results in higher dynamic moduli for stereocomplex polymers (IS-MMA, I-MMA-1, and I-MMA-2) than that for the syndiotactic polymer (S-MMA) over the entire temperature range.

Dynamic Viscoelasticity of Stereocomplex Polymers of Ethyl Acrylate and Methyl Acrylate

The loss tangent (tan δ) of blended polymers (S-EA and I-EA), copolymer (MMA-EA), and stereocomplex polymers (IS-EA-1 and IS-EA-2) is shown as a function of temperature in Figure 5. As indicated in Figure 5, the temperature dependence of tan δ for I-EA and S-EA shows the same maximum at about $-10°C$, which is attributed to α-process of poly(ethyl acrylate) (PEA). The rapid increases of tan δ observed at about 55°C and about 110°C are attributed to α-processes of isotactic and syndiotactic PMMA, respectively. This shows that in blended polymers the molecular motions of EA and MMA chains occur independently and that MMA chains are incompatible with EA chains.

On the other hand, in the copolymer (MMA-EA), only one rapid increase of tan δ is observed, at about 0°C. In the copolymer, EA chains and MMA chains are uniformly distributed throughout the polymer main chains, and, consequently, molecular motions of each chain occur synchronously. The facts that the copolymer (MMA-EA) is optically transparent and that the blended polymers (S-EA and I-EA) are optically opaque also suggest that in the copolymer and the blended polymers, EA chains and MMA chains are mixed homogeneously and heterogeneously, respectively, on the order of the optical wavelength.

In stereocomplex polymers (IS-EA-1 and IS-EA-2), the temperature of rapid increase in tan δ resulting from the motions of EA chains is lower than that in the copolymer MMA-EA by about 10°C and higher than those in the blended polymers (S-EA and I-EA) by about 10°C. This indicates that the restriction on the motions of the flexible EA chains by the rigid MMA chains increases in order of the blended polymers, stereocomplex polymers, and the copolymer. That is, EA chains and MMA chains are distributed in stereocomplex polymers more homogeneously than in the blended polymers but more heterogeneously than in the copolymer. The rapid increases in tan δ at about 50°C in I-EA and at about 110°C in S-EA result from micro-Brownian motions of isotactic and syndiotactic PMMA, respectively. If there were no special interactions between isotactic and syndiotactic PMMA, rapid increase
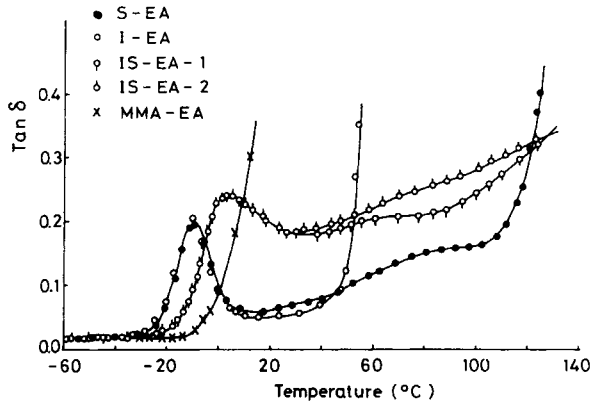
Fig. 5. Temperature dependence of tan δ for stereocomplex polymer, the blended polymers, and the copolymer of EA monomer.

in tan δ of stereocomplex polymers containing isotactic and syndiotactic PMMA should occur in a temperature range of 50°C to 100°C. However, there is no rapid increase in tan δ for stereocomplex polymers in this temperature region, which suggests that the molecular motions of the main chains of isotactic and syndiotactic PMMA are restricted by the steric complementary interactions between isotactic and syndiotactic PMMA. This is also supported by the studies on temperature dependence of dynamic modulus shown in Figure 6. In blended polymers (I-EA and S-EA), a two-stepped decrease of the dynamic modulus is clearly observed. The decrease at the lower temperature (about −20°C) is due to α-process of PEA, and the other rapid decreases at higher temperatures (about 60°C and 120°C) result from α-processes of isotactic and syndiotactic PMMA, respectively. In copolymer (MMA-EA), only one rapid decrease, which is attributed to α-process of the copolymer, is observed, at about −10°C. On the other hand, in stereocomplex polymer (IS-EA-2), the dynamic modulus decreases slowly above about
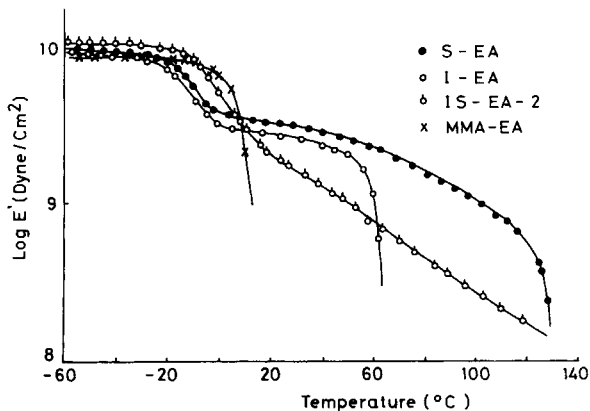

Fig. 6. Temperature dependence of the dynamic modulus of stereocomplex polymer, the blended polymer, and the copolymer of EA monomer.
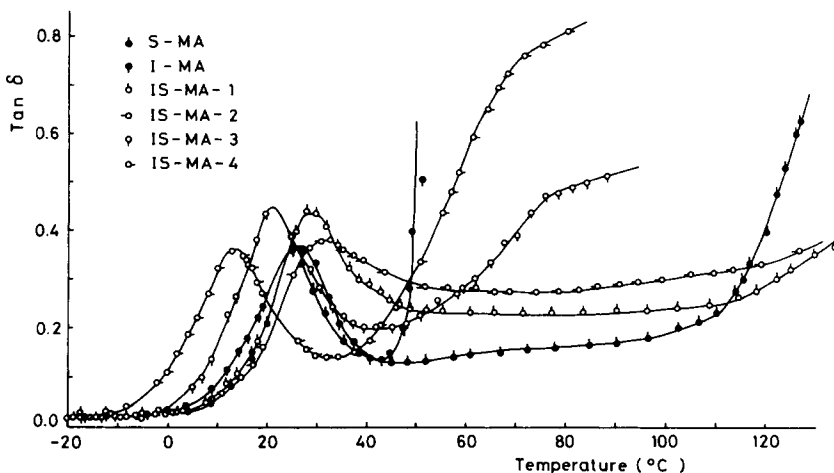
Fig. 7. Temperature dependence of tan δ for stereocomplex polymers and the blended polymers of MA monomer.

−10°C, and such rapid decreases as are observed in the blended polymers and the copolymer cannot be found.

These experimental data make it probable that, when EA monomer is polymerized under the conditions of stereocomplex association, the phase separation of the newly synthesized PEA molecules from a matrix of PMMA molecules can be restricted by the three-dimensional network structure resulting from the stereocomplex association between the isotactic and syndiotactic PMMA. Consequently, PEA molecules can be distributed homogeneously in the matrix of PMMA molecules. This is the reason why, in spite of being a kind of blended polymers, stereocomplex polymers have transparency like the copolymer and have different mechanical properties from those of the usual blended polymers and copolymers.

In Figure 7, is shown temperature dependence of tan δ of stereocomplex polymers of MA monomer with a variety of ratios of isotactic to syndiotactic PMMA. The temperature at the peak of tan δ owing to α-process of PMA varies with the ratio of isotactic to syndiotactic PMMA. In the usual blended polymers, free of isotactic PMMA (S-MA) and free of syndiotactic PMMA (I-MA), the peak temperature is the same, about 26°C. In stereocomplex polymers of MA monomer, the peak temperature is lowest (about 12°C) when the ratio is 5.0 and is highest (about 30°C) when the ratio is 0.2. On the other hand, in stereocomplex polymers of EA monomer, the peak temperature is lowest (about −10°C) in blended polymers (I-EA and S-EA) and highest (about 5°C) in stereocomplex polymers with the ratio in the range from 0.2 to 0.5. Temperature shift of the loss peak in tan δ of EA or MA chains to higher temperature region is thought to be related to the restriction on the molecular motion of EA or MA chains by coexisting rigid MMA chains and so is thought to be a criterion for uniformity of the mixture of MA or EA chains with MMA chains.

The glass transition temperature of PMA and PEA (0°C and −22°C)[19,20] is taken as a reference temperature from which the peak temperature shift is determined. That is the reason why at a glass transition temperature the

Ratio (Iso./Syn.)	Stereocomplex of EA, °C	Stereocomplex of MA, °C
Iso.	12	26
5.0	12	12
2.0	21	21
0.5	27	30
0.2	27	28
Syn.	12	26

micro-Brownian motions of PMA or PEA begin to occur in the state free of the restriction of rigid MMA chains. In stereocomplex polymers of MA and EA, the shifts of the peak temperatures from the respective glass transition temperatures are shown in Table III. The peak temperature shifts are identical (26°C) in the blended polymers of S-MA and I-MA and are also identical (12°C) in the blend polymers of S-EA and I-EA. This shows that there is no difference in the compatibilities of isotactic and syndiotactic MMA chain with EA chain and that also no difference in the compatibilities of isotactic and syndiotactic MMA chain with MA chain. The fact that the peak temperature shift in S-MA and I-MA is higher than that in S-EA and I-EA by 14°C suggests that MMA chain is more compatible with MA chain than with EA chain. Probably, the closer similarity of MMA chain to MA chain in chemical structure than to EA chain causes the better compatibility of MA chain with MMA chain.

On the other hand, if stereocomplex polymers have the same ratio of isotactic to syndiotactic PMMA, the values of the peak temperature shift of stereocomplex polymers of MA and EA are almost identical and yet are dependent only upon the ratio. When the ratio is from 0.2 to 0.5, at the compositions most suitable for the stereocomplex associations, the peak temperature shifts show maxima (27°C to 30°C). These results support the assertion that the uniformity of the mixtures of PMA or PEA with PMMA is not determined by the compatibilities of the each polymer with PMMA, but only by the density of the network structure, which is mainly dependent upon the ratio of isotactic to syndiotactic PMMA in stereocomplex polymers.

It is concluded that the network structure resulting from the stereocomplex association between isotactic and syndiotactic PMMA in gel state before polymerization prevents a phase separation of the newly created polymers from the matrix of PMMA during the polymerization process.

References

1. W. H. Watanabe, C. F. Ryan, P. C. Fleischer, and B. S. Garrett, *J. Phys. Chem.*, **65**, 896 (1961).
2. R. K. Graham, D. L. Dunkelberger, and J. R. Panchak, *J. Polym. Sci.*, **59**, 168 (1962).
3. D. L. Glusker, R. A. Galluccio, and R. A. Evans, *J. Amer. Chem., Soc.*, **86**, 187 (1964).
4. C. F. Ryan and P. C. Fleischer, *J. Phys. Chem.*, **69**, 3384 (1965).
5. R. Chiang, J. J. Burke, J. O. Threlkeld, and T. A. Orofino, *J. Phys. Chem.*, **70**, 3591 (1966).

6. A. M. Liquori, G. Anizuino, V. M. Coiro, M. D'Alagni, P. De Santis, and M. Savino, *Nature*, **206,** 358 (1965).

7. A. M. Liquori, M. Savino, and M. D'Alagni, *J. Polym. Sci. B,* **4,** 943 (1966).

8. H. Z. Liu and K. Liu, *Macromolecules,* **1,** 157 (1968).

9. A. M. Liquori, G. Anzuino, and M. D'Alagni, *J. Polym. Sci. A-2,* **6,** 509 (1968).

10. J. Dayantis, C. Reiss, and H. Benoit, *Macromol. Chem.,* **120,** 113 (1968).

11. T. Miyamoto and H. Inagaki, *Polym. J.,* **1,** 46 (1970).

12. A. Yu. Koshevnik, M. M. Kusakov, N. M. Lubman, L. I. Mekenitaskaya, O. V. Orlova, A. A. Pasynskaya, E. A. Razumovskaya, and L. M. Schul'pina *Vysokomol, Soedin.,* **A12,** 2103 (1970).

13. S. Fujishige, P. Goeldi, and H. G. Elias, *J. Macromol. Sci., Chem.,* **5,** 1011 (1971).

14. W. Borchard, M. Pyrlik, and G. Rehage, *Makromol. Chem.,* **145,** 169 (1971).

15. F. A. Bovey and G. V. D. Tiers, *J. Polym. Sci.,* **44,** 173 (1960).

16. E. A. W. Hoff, D. W. Robinson, and A. H. Willbourn, *J. Polym. Sci.,* **18,** 161 (1955).

17. K. Deutsch, E. A. W. Hoff, and W. Reddish, *J. Polym. Sci.,* **13,** 565 (1954).

18. S. Krause and N. Roman, *J. Polym. Sci. A,* **3,** 1631 (1965).

19. R. H. Gerke, *J. Polym. Sci.,* **13,** 295 (1954).

20. J. A. Shetter, *J. Polym. Sci.,* **B1,** 209 (1963).