NOTE

On the Dissolution of Poly(γ-methyl L-glutamate) in a Mixed Solvent of Benzene and Methanol

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It is well known[1] that poly(γ-methyl L-glutamate) (PMLG) is soluble in organic chloride solvents such as dichloromethane, dichloroethane, chloroform etc. when it has the conformation of an α-helix, and soluble in dichloroacetic acid (DCAA), trifluoroacetic acid etc. when in the formation of a random coil. However, this compound is hardly soluble in a single solvent such as a hydrocarbon or an alcohol.

The authors found that benzene dissolved PMLG when mixed with 5 to 30 wt% of methanol at a temperature above the boiling points of the components of this mixtures. Therefore, some of the experimental results on a PMLG solution containing this solvent mixture and the PMLG film prepared from this solution are reported in this paper.

SAMPLE

The PMLG used in this study was obtained from Ajicoat-A2000, supplied by Ajinomoto Co., Inc. Its molecular weight (M_v) was determined as 175,000 from a viscosity measurement in DCAA by the equation,[2]

$$[\eta] = 20.2 \times 10^{-5} \, M_v^{0.73}$$

RESULTS AND DISCUSSION

In general, the PMLG solid prepared by casting from its solution did not dissolve again in a helical solvent since the PMLG solid contained a small number of β-coil conformational chains which

formed by an effect similar to the denaturation of poly peptides.[1] However, PMLG cast without drawing from Ajicoat-A2000; *i.e.*, the solution of PMLG in a mixed solvent of 1,2-dichloroethane (DCE) and perchloroethylene (PCE) (7:3), was dissolved in benzene mixed with 5 to 30 wt% methanol at a temperature well above the boiling points of these constituents, as well as that of DCE–PCE and other helical solvents. Any small amount of PCE remaining in the PMLG film was dissolved at an ordinary temperature into the mixture.

The solution of PMLG in a mixed solvent of benzene and methanol, on being cooled down 1°C at a time, became transparent mass gells at gelation temperatures which changed with concentration of polymer and the ratio of methanol to benzene in the solvent. But when these gels were warmed up 1°C at a time, they became sols having low viscosity at solation temperatures about 10 to 15°C higher than the respective gelation temperatures. This phenomenon is similar to that of agar, gelatin etc. in water.

The relation between the gelation or the solation temperature and the concentration of methanol in the mixed solvent is shown in Figures 1 and 2, respectively, along with the parameter of the PMLG concentration. Each curve has a minimum temperatures at a concentration of about 15 wt% methanol, indicating that the mixture in this ratio has the largest solubility among these mixtures.

The dependence of the reduced viscosity of this mixed solvent solution on th PMLG concentration is shown in Figure 3, wherein the results for solutions
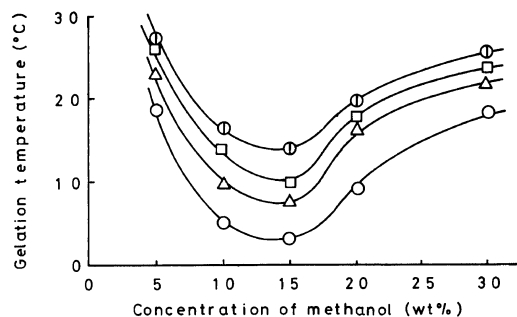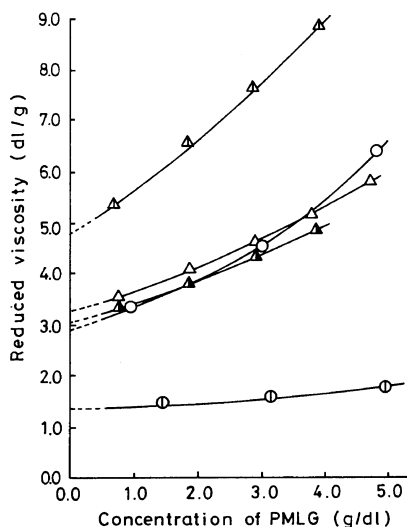
Figure 1. Relations between the gelation temperature and the concentration of methanol in benzene–methanol mixture for various PMLG concentrations of 1 wt% (○), 3 wt% (△), 5 wt% (□), and 7 wt% (◐).
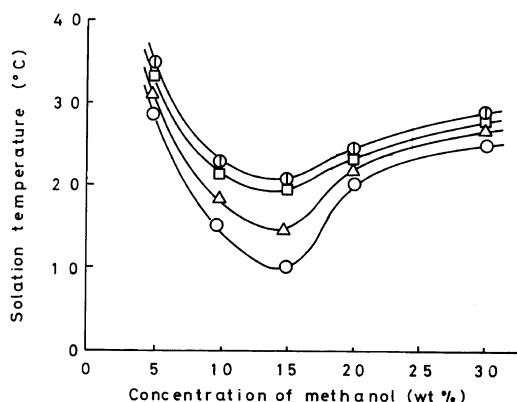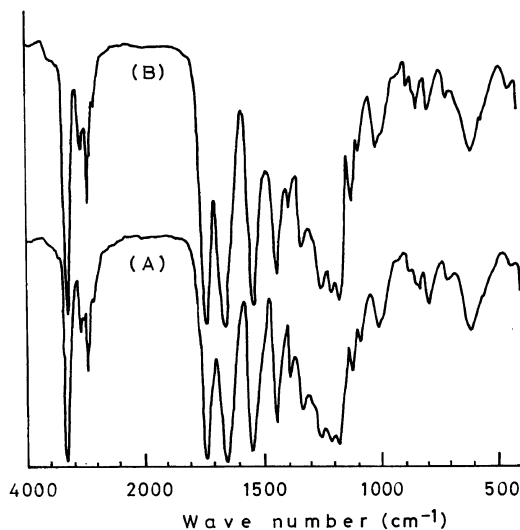

Figure 2. Relations between the solation temperature and the concentration of methanol in benzene–methanol mixture for various PMLG concentrations of 1 wt% (○), 3 wt% (△), 5 wt% (□), and 7 wt% (◐).

Figure 3. Concentration dependence of reduced viscosities of PMLG solutions in benzene–methanol mixture of 6 wt% methanol (⬭), 15 wt% (△), 25 wt% (▲), DCE–PCE (α-helical solvent) (○), and DCAA (random coil solvent) (◐).

Figure 4. IR spectra of the PMLG films cast from the solutions in benzene–methanol mixture (15 wt% methanol) (A) and DCE–PCE (B).

made with DCE–PCE (α-helical solvent) and DCAA (random coil solvent), respectively, are also shown for comparison.

As can be seen in the figure, the viscosity of the benzene–methanol solution of PMLG is closely related to that of the DCE–PCE solution. Doty *et al.*[3] measured the intrinsic viscosities of poly(γ-benzyl L-glutamate), and found a much higher viscosity value in solvents such as chloroform than in DCAA, and it was supposed that the polypeptides took on a helical conformation in the former solvents through intramolecular hydrogen bonding. It may be that PMLG mainly takes on the helical conformation in the benzene–methanol sol-
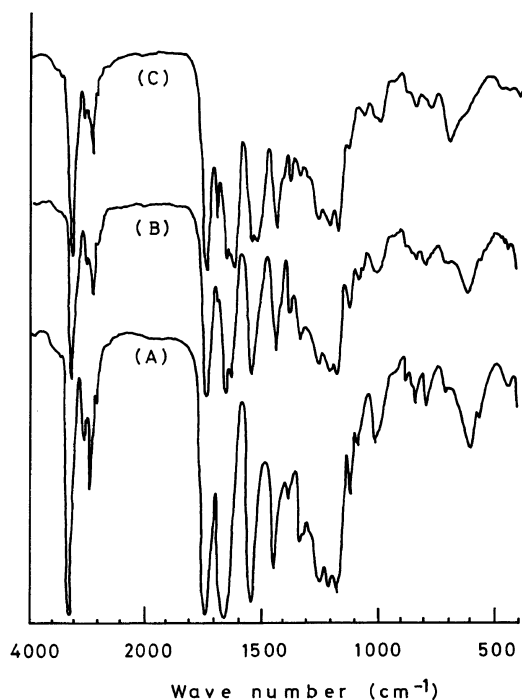
vent, though it is necessary to confirm this by other measurements employing the ORD or CD method. The intrinsic viscosities of the PMLG solution in these mixed solvents of 6 and 25 wt% in methanol

Figure 5. IR spectra of non-treated (A) 400% elongated (B), and formic acid treated (C), PMLG films. These films were cast from the solution of benzene–methanol mixture (15 wt% methanol).

content, show similar gelation temperatures for each other in Figure 1, and were 4.7 and 3.1 dl g^{-1} respectively. The viscosity of PMLG in a 15 wt% methanol solution lies between these two values. It is considered that the helix content of PMLG in this mixed solvent increases with benzene content.

The PMLG film prepared by casting from this solution was transparent. The IR spectrum of this film showed characteristic absorption bands of 1650 cm^{-1} (amide I), 1545 cm^{-1} (amide II), and 615 cm^{-1} (amide V) of the α-helical conformation shown in Figure 4.

What is of interest is that when the non-treated film was cut off with scissors and dissolved in a helical solvent, the cut-off section of the film remained insoluble as a thready residue. The film which was then frozen in liquid nitrogen and

fractured but dissolved completely without the formation of any residues. This phenomenon can be understood reasonably by considering that molecular chains of PMLG in the cut-off section are oriented by sheering stress when the films were cut with scissors and are transformed into the β-coil conformation.

The PMLG film was capable of being dissolved again in helical solvents and the mixed solvent, but when elongated by 50% in the dry state, the film became insoluble in any solvent[4] except for the random coil solvent. By treating this elongated and insoluble film with formic acid for 3 hours, the α-helical conformation transformed completely into the β-coil formation[5] shown in Figure 5(C).

The film was elongated 400% with boiling water, since an elongation to this extent was too difficult in the dry state, as a result the characteristic IR absorption bands of 1650, 1545, and 615 cm^{-1} of the α-helical conformation shifted partially to 1630, 1530, and 700 cm^{-1} of the β-coil conformation,[6] respectively, as shown in Figure 5(A) and (B). This suggests that the helical conformation of the component polymer chains transformed partially to the β-coil conformation. Based on these results, it is considered that PMLG dissolves in a benzene and methanol mixture, taking on mainly the α-helical conformation. This conformation in solution is still being kept in the film cast from the solution.

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