Physical Properties of Mixtures of Poly(γ -benzyl-L-glutamate) and Poly(γ -benzyl-D-glutamate)

Takao FUKUZAWA and Ichitaro UEMATSU*

*Department of Polymer Chemistry, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo, Japan.*

Yoshiko UEMATSU

*Department of Industrial Chemistry, Tokyo Institute of Photography,
Iiyama, Atsugi, Japan.*

(Received March 26, 1974)

ABSTRACT: It has been reported that there is a special side chain—side chain interaction between the right-handed and left-handed α -helices in the racemic mixture of poly(γ -benzyl glutamate). In this paper physical properties of mixtures of poly(γ -benzyl-L-glutamate) and poly(γ -benzyl-D-glutamate) are studied. From X-ray diffraction measurements, the reflection characteristic of the regular arrangement of the benzyl group at the end of the side chain was shown to disappear on heating at 97°C and to appear on cooling at 73°C. This reversible change was also observed in viscoelastic, thermal and dilatometric measurements and was ascribed to the breakdown and formation of stacks of benzene rings. In the case of samples cast from benzene solution, it was found that the formation of stacks is hampered by the preferable superhelix formation.

KEY WORDS Racemic Mixture / Poly(γ -benzyl glutamate) / Stack /
First-Order Transition / Physical Properties /

Some interesting differences have been reported between the X-ray diffraction patterns of the enantiomorphic and racemic forms of poly(γ -benzyl glutamate) (PBG). The enantiomorphic form of PBG, apart from some very weak reflections, is accounted for by an α -helical structure. In the racemic form of PBG, which is an equimolar mixture of poly(γ -benzyl-L-glutamate) (PBLG) and Poly(γ -benzyl-D-glutamate) (PBDG), although the pattern is very similar to that of an α -helix, there are many indications that the structure is distorted. In particular a meridional reflection appears at about 10.5 Å, whereas with an α -helix no meridional reflections corresponding to spacings greater than 1.5 Å should appear. The 10.5 Å reflection in the racemic form has been interpreted by Tsuboi, *et al.*,¹ as due to a pairing of D and L residues, with a special side-chain interaction which causes a regular arrangement of the benzyl group at the end of the side chain and simultaneously distorts the helix so that

the α -helix backbone is not a simple 18/5 α -helix with a repeat of 27 Å.

In a previous paper² we reported the presence of a special interaction in the side chains of PBG, and it was ascribed to stacks of benzene rings at the end of side chains. These stacks of benzene rings were considered to be caused by casting films from solutions in relatively poor solvents such as benzene or tetrahydrofuran, in which PBG molecules likely associate side by side to form superhelical aggregates. From viscoelastic and thermal measurements, we found an irreversible transition at 135°C and explained it in terms of the breakdown of stacks of benzene rings.

In this paper, we present some results of similar measurements for the mixture of PBLG and PBDG, which is considered to have a different arrangement of the side chain from pure PBLG.

EXPERIMENTAL

The PBG used in this study was prepared by

* To whom correspondence should be addressed.

polymerization of the *N*-carboxy anhydride of γ -benzyl glutamate, as described in a previous paper.² From viscosity measurements in dichloroacetic acid, the molecular weights of PBLG and PBDG were estimated to be 170,000 and 230,000 respectively. Films were cast from solution in dichloroethane (EDC) and benzene. Experimental measurements were carried out in the same way as reported in the previous paper.

RESULTS AND DISCUSSION

The intensity distributions of X-ray diffraction for the mixtures are shown in Figure 1. In the case of films cast from EDC, the reflection at $2\theta=6.8^\circ$ corresponding to $12.9\text{ \AA}$ for the (110) spacing, was the same as in pure PBLG, but a new reflection appeared near $2\theta=8.5^\circ$ corresponding to $10.3\text{ \AA}$. The intensity of this reflection gradually increased on increasing the PBDG fraction from 0% to 50%. This $10.3\text{-\AA}$ reflection corresponds to the $10.5\text{-\AA}$ reflection observed by Tsuboi, *et al.* In the case of film cast from benzene, the (110) reflection appeared near $2\theta=7.0^\circ$, was broader than that of film cast from EDC, and the $10.3\text{ \AA}$ reflection was not observed (in Figure 1 only the intensity distribution for the equimolar mixture is shown).

Figure 1. X-ray diffraction curves for the mixtures of PBLG and PBDG with various PBDG fractions, cast from EDC (a–f) and benzene (g): PBDG fractions, (a), 0; (b), 0.1; (c), 0.2; (d), 0.3; (e), 0.4; (f), (g), 0.5.

Figure 2. DTA thermograms on heating for the mixtures of PBLG and PBDG with various PBDG fractions, cast from EDC (a–e) and benzene (f, g): PBDG fraction, (a), 0.1; (b), 0.2; (c), 0.3; (d), 0.4; (e), 0.5; (f), 0.5; (g), 0.5, after annealed.

These results indicate that the arrangement of the side chain in the mixture is also affected by the casting solvent and that benzene has the effect of hampering the regular arrangement of the side chain in the mixture.

Differential thermal analysis (DTA) measurements on the mixtures were carried out at a heating rate of $10^\circ\text{C}/\text{min}$ and the results are shown in Figure 2. With films cast from EDC, the endothermic peak was observed near 90°C

Figure 3. DTA thermograms on cooling for the mixtures of PBLG and PBDG with various PBDG fractions, cast from EDC: PBDG fraction, (a), 0.1; (b), 0.2; (c), 0.3; (d), 0.4; (e), 0.5.

Figure 4. Heats of transition (○) and transition temperatures (●) for the mixtures of PBLG and PBDG.

on heating and shifted to higher temperature accompanied by an increase in peak height as the percentage of PBDG increased. The exothermic peak was observed near 50°C on cooling (Figure 3). In the case of film cast from benzene, the endothermic peak was observed at 135°C which seems to correspond to the transition observed in pure PBLG cast from benzene.² After annealing this film at 140°C for 5 min, the endothermic peak was observed at 95°C on heating. These results indicate that the above-mentioned effect of benzene is eliminated by heating to 140°C, that is, the structure formed by casting from benzene collapses at 135°C as in pure PBLG and the regular arrangement of the side chain proposed by Tsuboi, *et al.*, is formed.

In Figure 4 heats of transition obtained from endothermic peak areas and peak temperatures on heating are plotted against D-polymer content. Both quantities increased with increasing D-polymer content. For the equimolar racemic mixture the transition temperature was 95°C and the heat of transition was 4.4 cal/g, which is larger than the 2.9 cal/g for the transition observed at 135°C in pure PBLG cast from benzene. In this case the transition has been explained in terms of benzene-ring interactions or stacks in the side chains in the superhelical structure of PBLG. In contrast to the irreversible change of structure in pure PBLG cast from benzene, structural changes in the mixtures cast from EDC were reversible.

The storage tensile modulus E' and loss tangent $\tan \delta$ of the racemic mixture were measured at 110 Hz on heating and are plotted

Figure 5. E' and $\tan \delta$ as a function of temperature for the racemic mixture of PBG; 110 Hz, (●) cast from EDC, (○) cast from benzene.

against temperature in Figure 5. In the case of film cast from benzene, the dispersion observed around 50°C is considered to be due to the side-chain motion restricted by the interaction between benzene rings of the side chain in the superhelical structure. The presence of a superhelical structure in the mixture cast from benzene is considered to be rationalized

Figure 6. E' , E'' , and $\tan \delta$ as a function of temperature for the racemic mixture of PBG cast from EDC; (○) heating, (●) cooling.

by the abrupt change of modulus as well as a dispersion peak at 135°C. In conclusion, no differences in viscoelastic properties are observed between the racemic mixture and pure PBLG when cast from benzene solution. In the former the special benzene-ring interaction in the racemic mixture proposed by Tsuboi, *et al.*, takes place after heating to 140°C, while in the latter the heat treatment causes only the collapse of the benzene-ring interaction in the superhelical structure.

In the case of samples cast from EDC solution, a dispersion around 50°C was also observed, but a decrease of modulus was observed near 95°C, which is related to the endothermic peak observed in the DTA measurements. In Figure 6 the viscoelastic properties on heating are compared with the results on cooling. As already mentioned in relation to thermal measurements, reversible changes are also observed in the viscoelastic measurement. On cooling the moduli start to increase abruptly near 60°C and coincide with the values on heating.

The measurement of specific volume was carried out by dilatometry at the rate 1°C/3 min. In Figure 7 the temperature dependence of the specific volume for the racemic mixture both on heating and cooling is shown. The first-order transition is observed near 90°C on heating and

Figure 7. Specific volume vs. temperature curve for the racemic mixture of PBG; (○) heating, (●) cooling.

Figure 8. X-ray diffraction curves for the racemic mixture of PBG at various temperatures: on heating, (a), 20°C; (b), 50°C; (c), 70°C; (d), 97°C; (e), 110°C; on cooling, (f), 83°C; (g), 73°C; (h), 50°C; (i), 20°C.

near 70°C cooling. The transition near 90°C accompanied with hysteresis was also confirmed by X-ray diffraction studies. The intensity distributions of the X-ray diffraction for the racemic mixture at various temperatures are shown in Figure 8. The $2\theta=8.7^\circ$ reflection disappears at 97°C on heating and appears again at 73°C on cooling.

From these results, it is concluded that the transition observed at 90°C on heating for the racemic mixture of PBLG and PBDG is caused by a breakdown of the regular arrangement of the side chain.

CONCLUSION

Physical properties of the mixtures of PBLG and PBDG were studied. From viscoelastic, thermal, X-ray diffraction, and dilatometric measurements, we found a reversible transition at 95°C for the racemic mixture. This transition is considered to be related to the stacks of benzene rings at the end of side chains reported by Tsuboi, *et al.*, which are different in the structure from those in superhelical aggregates.

Physical Properties of Mixture of PBLG and PBDG

REFERENCES

1. Y. Mitsui, Y. Iitaka, and M. Tsuboi, *J. Mol. Biol.*, **24**, 15 (1967); J. M. Squire and A. Elliott, *ibid.*, **65**, 291 (1972).
2. T. Fukuzawa, I. Uematsu, and Y. Uematsu, *Polymer J.*, **6**, 431 (1974).