V. P. STESIKOV, Yu. V. OVCHINNIKOV, Academician V. A. KARGIN

1964

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

V. P. STESIKOV, Yu. V. OVCHINNIKOV, Academician V. A. KARGIN

THE INFLUENCE OF A NONSOLVENT ON THE PHYSICO-MECHANICAL PROPERTIES OF CONCENTRATED POLYMER SOLUTIONS

Concentrated solutions of high-molecular-weight compounds, one of whose components is a low-molecular-weight liquid, are of practical interest. According to current concepts ([1–4]), concentrated polymer solutions possess a structure either analogous to mixtures of two low-molecular-weight liquids, or the structure of a gel, with the spatial network structure characteristic of the latter, arising as a result of the formation of a sufficient number of strong intermolecular bonds.

In a number of papers by Kargin and co-workers ([5,6]) it was first shown with sufficient clarity that solutions of high-molecular-weight substances are reversible, thermodynamically equilibrium systems, and that the phase rule is applicable to them.

In the literature ([7–13]), the question of compatibility, i.e., the solubility of a low-molecular-weight liquid (plasticizer) in a polymer, has been discussed repeatedly. The preparation of a uniform, homogeneous mixture of a polymer and a low-molecular-weight substance is a very important problem from the standpoint of changing the physico-mechanical properties of the polymer.

A number of authors ([10–12]), in order to explain the limits of compatibility of a polymer with a low-molecular-weight liquid (plasticizer), used the phase-equilibrium diagram of the components. It was shown that the compatibility of a polymer with a plasticizer is determined by the phase-equilibrium curve on the composition–temperature diagram.

Papkov ([13]), considering a scheme for the change in the mechanical properties of the polymer–plasticizer system, explains the appearance of high reversible deformation of a plasticized polymer at a definite temperature and at definite component ratios by the transition of the system into the region of separation into two equilibrium phases with incomplete stratification (gel formation).

However, despite the large number of works devoted to the study of concentrated polymer solutions, some questions, in particular those connected with the mechanical properties of solutions, have still been insufficiently developed and not to such an extent that it would be possible to change these properties

Fig. 1

Figure 1: Fig. 1

in a directed way. The new concepts of the structure of amorphous polymers advanced in recent years and brilliantly confirmed by experiment (14–16), and, as a consequence, changes in views on the mechanism of plasticization (dissolution) of polymers (17,18), give grounds for assuming that the structural features of polymer substances should be distinctly manifested in solutions of high polymers and should to a considerable degree determine the physico-mechanical properties of the latter.

The aim of the present work is to show the possibility of changing, over a wide range, the mechanical properties of concentrated polymer solutions by changing the solvent power of the solvent.

The physico-mechanical properties investigated were the glass-transition temperature, tensile strength, and relative elongation at break of con—

centrifuged solutions of a copolymer of acrylonitrile with methyl acrylate, with the content of the second component in the copolymer being 20%. Propylene carbonate and its mixtures with dibutyl phthalate were used as the low-molecular solvent.

Pure propylene carbonate is a comparatively good solvent for the copolymer of this composition. The dissolving power of propylene carbonate was changed by adding to it dibutyl phthalate, which is a nonsolvent for the copolymer. The solutions were prepared at equal equivolume ratios of polymer to low-molecular liquid.

The powdered polymer was mixed with the solvent under continuous evacuation in a special mixer. The thoroughly homogenized dispersion (paste) was poured under vacuum into the appropriate sealed molds, after which the molds were kept at a temperature of 50° for 24 hours until a homogeneous polymer solution (gel) was formed.

The specimens thus prepared were tested for glass-transition temperature (T_c), tensile strength, and relative elongation at break.

Fig. 1. Dependence of tensile strength (σ) and relative elongation at break (ε) on the content of nonsolvent. 1 —tensile strength at stretching, 2 —relative elongation at break

The data presented in Fig. 1 on the influence of the amount of nonsolvent in the solution on strength and elongation show that, in the case of a good solvent, which pure propylene carbonate proves to be, the strength of the copolymer solution is considerably inferior to the strength of solutions prepared with a solvent-nonsolvent mixture. As the amount of dibutyl phthalate in the liquid mixture increases, the strength of the concentrated copolymer solutions increases.

Fig. 2

Figure 2: Fig. 2

Fig. 2. Dependence of the glass-transition temperature (T_c) on the content of nonsolvent

Noteworthy is the fact that, when the content in the propylene carbonate-dibutyl phthalate mixture is from 10 to 20%, the sharpest increase in the strength of the solutions is observed; at the same time the relative elongation remains practically at the same level up to a content of 20% dibutyl phthalate in the mixture.

When the content of dibutyl phthalate in the solution exceeds 20%, the tensile strength and relative elongation of the polymer solutions drop sharply, which is accompanied by noticeable syneresis of the low-molecular liquid, a cloudy appearance of the prepared specimens, and whitening of them during stretching; this indicates that the system has separated into two macroscopic phases.

It should be noted that, in the region of the sharpest increase in strength, no visible phase separation is yet observed—of the copolymer solution in the low-molecular liquid and of the liquid solution in the copolymer. The solution specimens before and after testing remain completely homogeneous and transparent.

Of considerable interest are the experimental data on the de—

dependence of the glass-transition temperature (T_c) of the solutions on the amount of added nonsolvent (Fig. 2). As can be seen from the figure, when the content of dibutyl phthalate in the mixture of liquids is up to 10%, the glass-transition temperatures of the concentrated copolymer solutions at one and the same volume ratio of polymer to low-molecular liquid differ, in essence, only slightly.

In the region of dibutyl phthalate concentrations of 10–20%, there is a sharp increase in the glass-transition temperature of the solutions, which, as we see, correlates fairly well with the strength data, which begins to increase more noticeably in the same concentration range.

It seems possible to interpret the experimental data obtained from the standpoint of modern ideas on the structure of polymers ([14–16]) and the existence of two types of plasticization—intracluster and intercluster ([17,18]).

Pure propylene carbonate and its mixtures with dibutyl phthalate, if the latter is present in an amount not exceeding 10%, are comparatively compatible with the polymer under study, owing to the fact that, upon dissolution, stronger intermolecular bonds are formed between the macromolecules and the molecules of the low-molecular solvent than the intermolecular bonds in the polymer itself.

The solvent, being distributed within the secondary structural formations (clusters) of the polymer, partially or completely destroys them and forms a uniform homogeneous polymer-solvent system; that is, in the present case one of the mechanisms of solvent (plasticizer) action is observed—intracluster.

An increase in the mixture to more than 10% dibutyl phthalate leads to a decrease in the dissolving power of the solvent, owing to the fact that the forces of intermolecular interaction in the copolymer predominate over the forces of interaction between polymer and low-molecular liquid. In this case it is quite obvious that the solvent will tend to be distributed between clusters of polymer chains and other secondary structural formations, and to a significantly lesser degree within them.

In other words, here we are dealing with the second mechanism of action of the solvent (plasticizer)—intercluster plasticization (dissolution); in this case the concentrated copolymer solution will be characterized by the presence of secondary structural formations—clusters of polymer chains.

On the basis of the foregoing, the reason for the difference in the physico-mechanical properties of the solutions at dibutyl phthalate concentrations up to and above 10% becomes clear. In the first case, when the low-molecular liquid is well compatible with the copolymer, the mechanical properties are determined by the primary structural units of the polymer—polymer chains; in the second case, the properties are governed by secondary structures—clusters of chains.

A noteworthy feature is that the transition from one mechanism of solvent action to the other occurs comparatively sharply within a small interval of change in dibutyl phthalate concentration. Correspondingly, those physico-mechanical properties of the concentrated solutions that are determined by their structural features (strength, glass-transition temperature) also change stepwise.

We noted above that in the region of the strength maximum (at a dibutyl phthalate concentration in the mixture of 10–20%) no visible separation of the solid phase of the polymer and the low-molecular liquid is observed, although it is precisely in this region that a distinctly expressed transition from one type of dissolution (plasticization) to the other takes place. This fact should apparently be explained by the low-molecular liquid being distributed both within the cluster space and in the intercluster regions, but with preferential distribution in the latter; that is, in the present case

there is microstratification of the system, but no separation into two macroscopic phases occurs.

We consider it especially necessary to note the fact that the presence in a polymer solution of secondary structural formations, even in the case where these structures are expressed quite clearly, in no way contradicts the phase rule; just as in the case of low-molecular-weight liquids, the presence of molecular associates gives no grounds for considering the liquid to be a two-phase system.

In our case, when the presence of secondary structures is characteristic of the polymer solution from the standpoint of the generally accepted concept of a phase, we are dealing with a single homogeneous phase; moreover, the sharp change in the physico-mechanical properties of the solutions is due not to the formation of a new phase, but to the formation of a qualitatively new supramolecular structure of the solution.

On the basis of the foregoing, one may conclude that, within one and the same phase, the physico-mechanical properties of polymer solutions vary significantly through changes in their supramolecular structure.

The very fact that physico-mechanical properties can be directionally changed by altering the solvent power of a low-molecular-weight liquid can undoubtedly be used in a number of special fields in which concentrated polymer solutions are applied (bonding, film formation, plasticized high-polymer plastics, etc.).

Received
28 XI 1963

REFERENCES CITED

1. A. A. Tager, *Solutions of High-Molecular Compounds*, 1959.
2. Yu. S. Lipatov, N. F. Proshlyakova, *Uspekhi khim.*, **30**, 517 (1961).
3. S. S. Voyutskii, *Solutions of High-Molecular Compounds*, Moscow, 1960.
4. V. A. Kargin, G. L. Slonimskii, *Brief Essays on the Physical Chemistry of Polymers*, Moscow, 1960.
5. S. P. Papkov, V. A. Kargin, Z. A. Rogovin, *ZhFKh*, **10**, 607 (1937); **13**, 206 (1939).
6. A. Tager, V. A. Kargin, *ZhFKh*, **15**, 1029 (1941).
7. Sh. L. Lel' chuk, V. I. Sedlis, *ZhPKh*, **31**, 887 (1958).
8. A. K. Doolottly, *K. Polim. Sci.*, **2**, 121 (1947).
9. V. A. Voskresenskii, L. M. Kozlov, *ZhPKh*, **33**, 191 (1960).
10. S. P. Papkov, *Promyshlennost' org. khim.*, **6**, 240 (1939).
11. H. M. Spurlin, A. F. Martin, H. G. Tennet, *J. Polim. Sci.*, **1**, 63 (1947).
12. R. S. Colborne, *Brit. Plastics*, **20**, 346 (1948).
13. S. P. Papkov, *Koll. zhurn.*, **19**, 722 (1957).
14. V. A. Kargin, A. I. Kitaigorodskii, G. L. Slonimskii, *Koll. zhurn.*, **19**, 131

(1957).

15. V. A. Kargin, N. F. Bakeev, *Koll. zhurn.*, **19**, 133 (1957).

16. V. A. Kargin, N. F. Bakeev, Kh. Vergin, *DAN*, **122**, 97 (1958).

17. V. A. Kargin, P. V. Kozlov, R. M. Asimova, *DAN*, **135**, 357 (1960).

18. P. V. Kozlov, R. M. Asimova, A. N. Perepelkin, *Vysokomolek. soed.*, **4**, 124 (1962).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.