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Phase and conformational transitions in the polyvinyl chloride–butanone-2 system

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SUMMARY

By studying optical densities in the visible region of the spectrum and the optical densities of infrared absorption bands, the structural and conformational states of the PVC - butanone-2 system were investigated. This system has a crystalline equilibrium and it is characterized by the formation of molecular complexes in solution. We observed two types of gel formed when the chemical equilibrium for the reaction of complexes formation is shifted by the evaporation of the solvent. It is shown that when PVC is dissolved, one type of supramolecular structure is broken down and another type is formed due to the stabilization of non-equilibrium PVC conformations by solvation.

INTRODUCTION

Although PVC is a well studied commercial polymer, many of its properties nevertheless remain unclear. This is particularly true of the phase structures of its mixtures with solvents, plasticizers, or other polymers (I-4). We may even say that the contradictions between the data on the compatibility of PVC with various other components is primarily due to the variegated physiochemical properties of PVC itself, as it has a complicated hierarchy of structures. Thus it has been shown in (2) that PVC has two typical crystal types, viz.,scaly and micellar, the latter only being observed if the system is formed via a gel stage. Many complicated phenomena of phase separations, gel formation, and so on demand a more detailed examination of the relationships between phase equilibria and the structural components observed in PVC mixtures. In this paper we study the phase equilibria and conformation transition of a PVC - solvent system, the solvent we took being butanone-2, which is widely used in the investigation of PVC's compatibility with other polymers.

EXPERIMENTAL

The phase and conformational states of the PVC - butanone-2 system were studied over a wide range of concentrations from powdered PVC through its solution in butanone-2 to PVC film. We used commercial C-70 PVC ($MM = I.4 \cdot IO^5$, $M_w/M_n = 2$) and purified desiccated and distilled butanone-2 (b.p. = 352K, $n_d = I.3786$).

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The phase structure of the solution was studied for temperatures between room temperature and the solvent's boiling point by the cloud point method using a G-III Carl Zeiss microphotometer. To obtain the solubility curves mixtures of powdered PVC and butanone-2 were placed in a sealed cuvette which was then put into the temperature controlled cell of the microphotometer and heated in steps up to the temperature T_m at which the turbid system turned clear.

The temperature-concentration curves for gelation ($T_{gel} - \omega'$) were determined by a similar technique but in this case the solvent was isothermally evaporated until there is a step change in the solution's transparency (note that the transparency rises rapidly at the gelation point). Then the cuvette was capped and weighed. The relative errors of the two experiment procedures ranged from 5 to 7%.

The IR absorption spectra of PVC were measured at room temperature with a G 983 Perkin-Elmer spectrometer at 500 to 700 cm^{-I}. This frequency corresponds to C-Cl stretching vibrations, which are sensitive to the PVC macromolecule's conformations (5,6). PVC is known to change conformation due to external influences (5,7), therefore the powdered PVC was studied without any pretreatment by the diffuse reflection technique. The spectrometer resolution between 500 and 700 cm^{-I} was 3 cm^{-I}.

RESULTS AND DISCUSSION

Butanone-2 did not dissolve powdered PVC for a period of many days until heated to a temperature T_m. At this point the swollen system suddenly dissolves which is evidenced by a sharp change in its transparency. Although the crystallinity of C-70 PVC is not high (7 to 8% according to calorimetric data), it is obvious that the swollen crystalline network formed during the polymer's synthesis is melted. The way the melting point depends on concentration ($T_m - \omega$) is presented in Fig.I (curve I). The curve is described by Flory's equation (8):

$$(I) \qquad I/T_m - I/T_{m_o} = RV_u/\Delta HV_I \,(\varphi_I - \chi_{I2}\varphi_I^2 - \ln\varphi_2/x)$$

where T_{m_o} is the melting point of pure PVC; T_m is the melting point of PVC with a volume fraction φ_2; V_I is the molar volume of the solvent; V_u is the molar volume of the repeating unit; ΔH is the latent heat of melting of the repeating unit in the polymer molecule (2.7 kcal/monom. for PVC (I)); and x is the degree of polymerization. Using experimental values of φ_2 and T_m (Fig.I, curve I) and equation (I) the interaction parameters χ_{I2} were calculated for PVC and butanone-2 (Fig.2). Using values of χ_{I2} found by extrapolating the line in Fig.2 into the high-temperature region the full melting curve was calculated from equation (I) (Fig.I, dotted line). The small and negative values of χ_{I2} suggest that there are some specific interactions in the system.

In fact, it was found that when a solution obtained by heating is cooled to room temperature (the A $\longrightarrow$ B transition in the diagram), no phase separation is observed. However, concentrating these solutions (the A $\longrightarrow$ D or B $\longrightarrow$ C transitions) brings about gelation. We have determined that the gel is lyotropic and thixotropic. The onset of gelation coincides with the step increase in the solution's transparency (Fig.3), which occurs for a particular composition (ω') at the point marking the gelation threshold. Note that $\omega' \gg \omega^*$ (ω^* is the concentration of overlapping of PVC molecular coils). Special measurements of ω' at various temperatures showed that the position of the gelation threshold on the concentration scale does not depend on temperature (Fig.I, curve 2).

It can be seen from a comparison of curves I and 2 in Fig.I that, even though they were similarly obtained, melting and gelation curves ($T_m - \omega$ and $T_{gel} - \omega'$, respectively) are not identical. It is evident from the slope of curve 2 in Fig.I that according to the equation $\ln c = \Delta H_{gel}/RT - \mathrm{Const}$, the network energy in the gel (ΔH_{gel}) is close to zero. Accordingly, the gelation results from a weak dispersive interaction rather than from PVC crystallization. This is also suggested by the fact that the system becomes more transparent at the gelation point (and not the reverse). Finally, a direct IR spectroscopic study of the PVC - butanone-2 system demonstrated that the PVC spectra of a 3% solution and a 25% gel (adjacent to ω') are identical (Fig.4c, curves I,2) and contain no 605 and 640 cm^{-1} bands, which would be ascribed to crystalline PVC (9). It should be pointed out that the literature has other examples of thermally reversible dilute PVC gels (e.g., in dioxane) that are formed by dispersive or other weak interactions and examples that experimental temperatures and those calculated by the Flory-Huggins theory for the gel-sol transitions do not coincide (IO, II). On the other hand, it is known that PVC molecules in solution are associated (I2). It is believed that the observed step change in the transparency and the parallel gelation is caused by the formation of finite-size associates within a single infinite cluster.

Thus the experimental data indicate that when a fairly dilute solution obtained by heating passes through the melting curve (cooling or concentrating) tHere is no phase separation in the system.

Effects typical of block-polymers, of which PVC is one because of its mixed iso- and syndiotactic structure, are usually attributed to the kinetic inhibition of phase separation processes due to the formation of a microcrystal gel network (I,2,8). However, the gelation is shown (Fig.I) to take place away from the melting curve and not to be caused by PVC crystallization. In this case, the properties of the system cannot be interpreted in terms of the generally adopted mechanism of gelation and phase separation inhibition in a PVC solution. The curve χ_{I2} (Fig.2) and the published data (I2) suggest a specific PVC- butanone-2 interaction which is probably responsible for the phase and morphological structure of the system. This fact has been ignored so far in discussions of the phase and structural states of systems incorporating PVC.

Let us now discuss the IR evidence. The spectra of powdered PVC and films obtained from solution are presented in

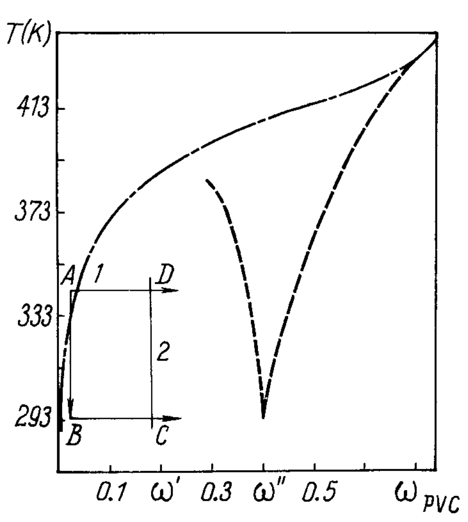


Fig. I

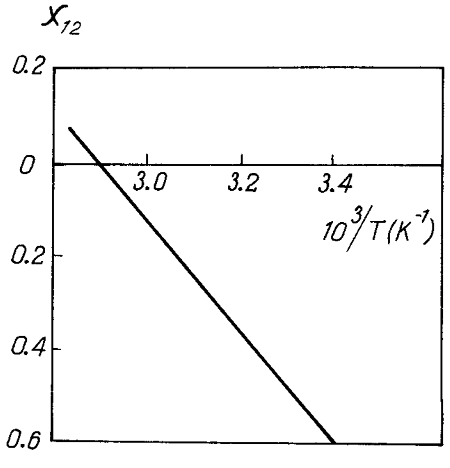


Fig. 2

Fig. I Temperature-concentration curves for (I) solubility (T_m - ω) and (2) gelation(T_{gel} - ω'). The solid line is experimental, the dot-dash line is a theoretical curve derived by eqn. (I), dashed line, see text.

Fig. 2 Temperature dependence of the PVC - butanone-2 interaction parameter (χ_{12}) calculated from the experimental melting curve (curve I in Fig.I).

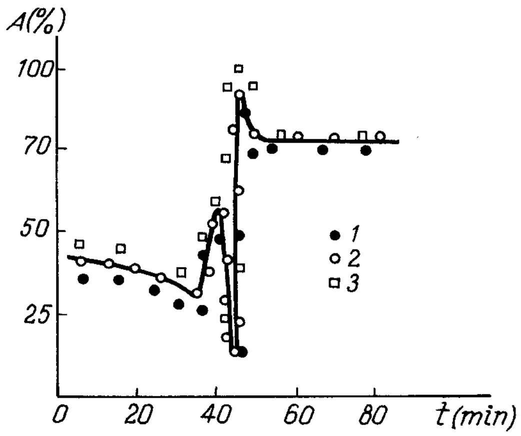


Fig. 3 Typical time-light transmission curve for PVC - butanone-2 mixtures during solvent evaporation under isothermal conditions at the temperatures: (I) 293 K, (2) 333 K, (3) 343 K.

Figs.4 a,b. The spectra are substantially different, and although this difference has been known for a long time (7, 9, I3), no satisfactory explanation has been provided. The situation not only presents difficulties in the interpretation of the spectra but frequently yields arbitrary results. As can be seen from Fig.4a, the spectrum of powdered PVC has two extra groups of bands, each of which contains several components. The first group (600 to 650 cm^{-I}) (I) contains bands at 605, 620 and 640 cm^{-I} and the second one (670 to 700 cm^{-I}) (II) contains bands at 685 and 693 cm^{-I}. The 605 and 640 cm^{-I} bands characterize long planar (the TTTT conformation) syndiotactic sequences and, as was mentioned above, are present in the IR spectra of the crystalline samples (9). The 693 cm^{-I} band corresponds to folded TTG*G* syndiotactic conformations(6). The 620 cm^{-I} band corresponds to extended TGTTGT conformations and the 685 cm^{-I} band to helical TGTGTG conformations of the isotactic chain sequence.(6).

The IR spectra of films (Fig.4b) obtained from solution in butanone-2 (similar results are obtained when other solvents and plasticizers are used (I3, I5)) are radically different. They include bands at 6I6 and 637 cm^{-I} in group I and a 693 cm^{-I} in group II. The intensities of the bands in the two groups are noticeably redistributed ($D_I/D_{II} \simeq I$ in powder PVC and $\simeq I.7$ in the films).Figure 4 also contains the spectrum of a film obtained from a solution of PVC in TGF, which we used as a good solvent.

When studying the range of PVC - butanone-2 systems from solution systems to film systems (Fig.4c), the 637 cm^{-I} band was found to be present in the IR spectra of PVC solutions, but only in the form of a shoulder. The band becomes distinct at a certain concentration ω'' (Fig.4c, curve 3) when, we have observed, the gel appearing in the system at ω' loses its lyotropic and thixotropic properties to become elastic. It follows from this that the 637 cm^{-I} band characterizes intermolecular interactions in the condensed state. It is obvious that the type of intermolecular packing in the film after the removal of solvent differs from the packing which occurs when the PVC is synthsized (Figs.4 a,b). We denote synthesized PVC as PVC(I) and the solution obtained from it as PVC(2).

We now turn to a discussion of the transformations of PVC(I) when it dissolves and why, when passing through the melting curve (Fig.I, curve I), no phase separation occurs to restore the initial phase structure up to the glass transition point of the system.

The IR spectra indicate that during the dissolution of PVC not only are the crystalline and helical structures of PVC(I) destroyed, which is suggested by the absence of the 605, 640 and 685 cm^{-I} bands (Fig.4b), but the macromolecule conformations are significantly changed, the stable extended TTTT conformations of the syndiotactic sequences converting to short TT and unstable TTTG conformations, and the stable helical conformations of the isotactic sequences converting to unstable TGTG*TG conformations. The short TT conformations (at 6I2 cm^{-I}) together with a shifted 620 cm^{-I} band appear in the spectra of the solutions as the6I6 cm^{-I} band (I3) and the unstable isotactic and syndiotactic conformations appear as a 637 cm^{-I} shoulder (see (5, 6, I3)).

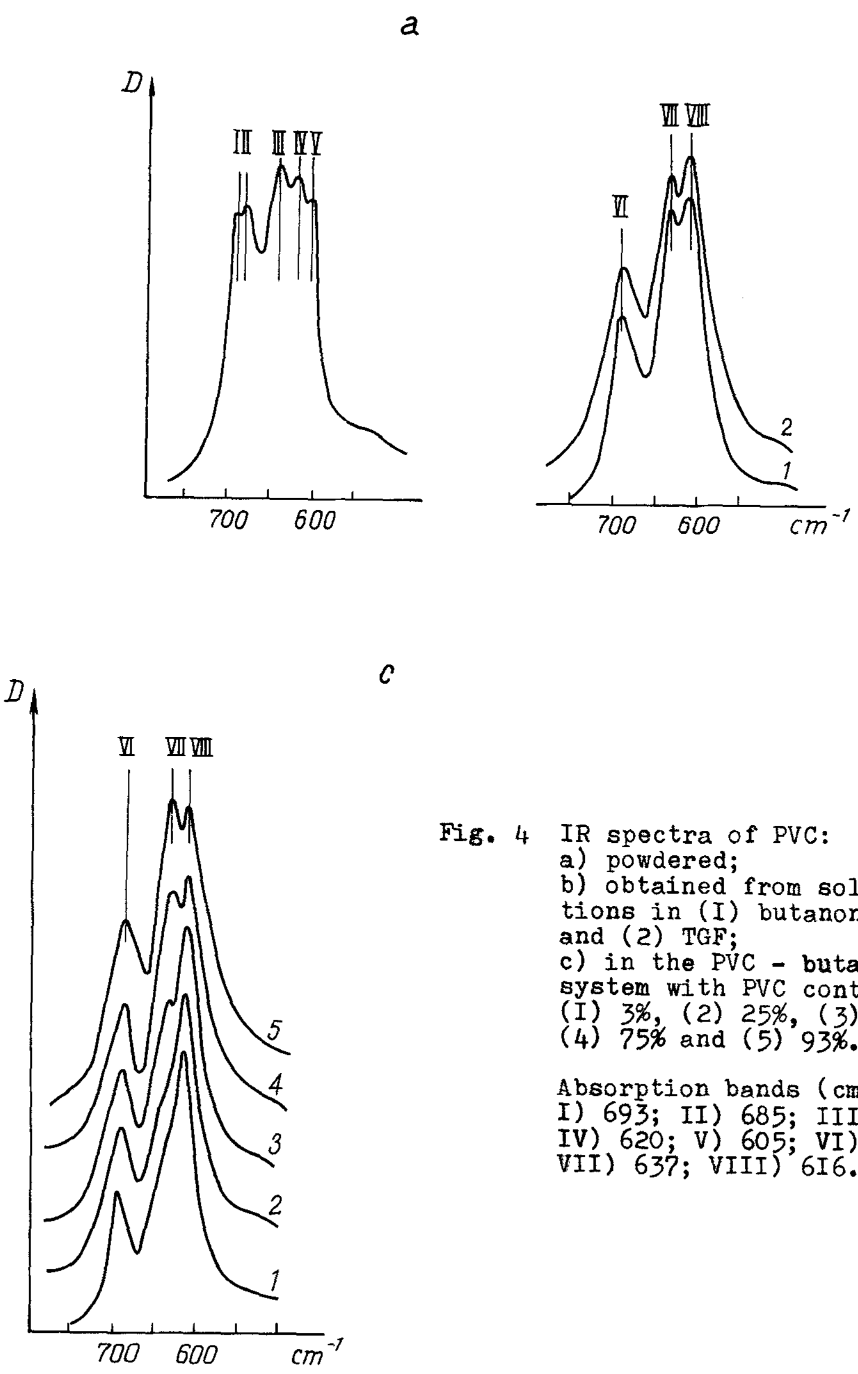
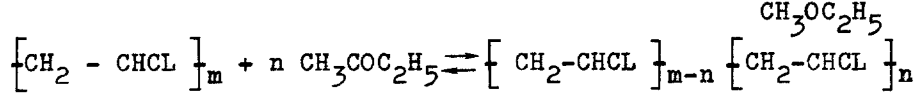


Fig. 4 IR spectra of PVC:
a) powdered;
b) obtained from solutions in (I) butanone-2 and (2) TGF;
c) in the PVC - butanone-2 system with PVC contents: (I) 3%, (2) 25%, (3) 40%, (4) 75% and (5) 93%.

Absorption bands (cm^{-I}): I) 693; II) 685; III) 640; IV) 620; V) 605; VI) 693; VII) 637; VIII) 6I6.

In addition, the presence of the 637 cm^{-I} shoulder in the spectra of the solutions and gels near ω' instead of a resolved band, which is typical of films (Figs.4 b,c) (I2), points to the fact that PVC molecules are solvated, the complex appearing on the unstable PVC conformations (637 cm^{-1}). Thus when dissolved in butanone-2, the PVC(I) macromolecules become perturbed which is stabilized by a reaction with the solvent and this is maintained until a solid PVC(2) film is formed.

The experimental data, taken as a whole indicates the following equilibrium picture. The melting and dissolution of powdered PVC(I) involves the destruction of the stable conformations and the stabilization of their modified forms. Thus we have the establishment of the chemical equilibrium:



$$\left[CH_2 - CHCL\right]_m + n\ CH_3COC_2H_5 \rightleftharpoons \left[CH_2\text{-}CHCL\right]_{m-n}\left[\overset{CH_3OC_2H_5}{CH_2\text{-}CHCL}\right]_n$$

In this case the phase equilibrium of the PVC - butanone-2 system can be described by a diagram typical of a system containing intermediate components. The melting curve in this case should have the form shown in Fig.I by a dashed line. It is evident that the lyotropic gel appears in the portion of the diagram with excess solvent, and the equilibrium is shifted to the right towards greater solvate formation. Hence, the gelation threshold ω' is characterized by concentration of the solvated PVC units, which is likely to control its displacement towards $\omega' \gg \omega^*$. Concentrating a solution shifts the equilibrium towards free PVC units, and the gelation point ω'' (Fig.4c, curve 3) is likely to correspond to bond redistribution at the lattice sites of a continuous network of molecular complexes.

CONCLUSIONS

The PVC - butanone-2 system is shown to have a crystalline equilibrium with the formation of molecular complexes in solution. The dissolution of PVC in butanone-2 and other solvents leads to the destruction of one structural type, solid PVC(I) and the formationof a new PVC(2) due to the stabilization of nonequilibrium conformations with a solvent up to the glass transition of the system. Thus the films obtained from solution remain in the perturbed conformational state, which is not in equilibrium in the absence of a solvent. The formation of micellar crystals in PVC(2) that passes through the gelation stage has a conformational nature as described above and results from the transition of the system to the new equilibrium state.

Two types of gel distinguished by weak and strong molecular interactions (ω' and ω'', respectively) but with the same physical state have been found, as distinct from the established types which have different states (I6). The gelation mechanism in the PVC - butanone-2 system (and, probably, in other PVC - solvent systems) is characterized by specific interactions and is controlled by shifts in the chemical equilibria between the solvated and unsolvated macromolecules as the solvent is evaporated. It is obvious that if several of the phenomena observed in temperature-concentration space of the phase diagram occur at the same time, a more sophisticated construction of the phase space that takes into account structural -conformational transitions of the type PVC(I) → PVC(2) will be necessary (especially for binary polymer - polymer blends obtained from solution).

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