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Thermoreversible Gelation of Poly(vinylidene fluoride) – Camphor System

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Summary: Poly (vinylidene fluoride) (PVF_2) produces thermoreversible gel in camphor when quenched to 25^0C from the melt under sealed condition. The SEM micrograph of dried PVF_2/camphor gel ($W_{PVF_2} = 0.25$) indicates presence of fibrillar network structure and the gels at different composition shows reversible first order phase transition. The phase diagram of the gel suggest the formation of a polymer- solvent complex. The melting enthalpy gives a stoichiometric composition of the complex at $W_{PVF_2} = 0.25$. This corresponds to a molar ratio of *PVF_2 monomer/camphor* ≈4/5. Temperature-dependent synchroton experiments further support the conclusions derived from the phase diagram.

Keywords: camphor; phase diagram; polymer solvent complex; poly (vinylidene fluoride); thermoreversible gel

Introduction

Thermoreversible gels have been extensively studied for the last two decades [1-3]. Poly(vinylidene fluoride) (PVF_2) is a technologically important polymer and produces thermoreversible gels in different solvents containing >C=O group such as diesters [4-7]. Extensive studies of the physical properties of the PVF_2 gels were made for diesters of varying intermittent length [7]. The thermoreversible PVF_2 gels display a three dimensional fibrillar network structure. Keeping this network structure unaltered is important in dried gels that can be used as porous material. However, the drying of these gels while keeping intact the original network structure is a difficult task. In this aim, we have studied PVF_2/camphor systems, that produce thermoreversible gels. The advantage of camphor lies in its propensity of sublimating easily so that solvent removal occurs under near "freeze-drying" conditions. In this short paper we report on the morphology, the thermodynamics (phase diagram) and the crystalline structures of these gels.

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Experimental

Poly(vinylidene fluoride) (PVF_2) is a product of Aldrich Chemical Company Inc. The weight average molecular weight ($\overline{M}_w$) of the sample is 180 000 g/mol and polydispersity index is 2.54 as obtained from GPC. The PVF_2 sample was recrystallized from its 0.2% (W/V) solution in acetophenone. Camphor was purified by sublimation procedure.

The PVF_2 and camphor were taken in a thick walled glass tube (8 mm in diameter) and were sealed under vacuum(10^{-3} mm Hg). The sealed tubes were melted at 210 ^{0}C in an oven for 20 min with intermittent shaking to make homogeneous. They were then quenched to 30 ^{0}C. For SEM study the samples were taken out from the tube and kept in a vacuum for 2 days. It was then gold coated and was then observed in a SEM apparatus (Hitachi S-415 A). For temperature dependent X ray investigation gels were prepared by melt quenched method as above and were then cut into circular sample of diameter 4 mm and placed into an equal size window of an aluminum holder, both sides were glued with mica of thickness 25 micron to prevent solvent evaporation. The data were taken at the Synchroton X-ray radiation facility (ESRF) at Grenoble, France, on D2AM beam line.

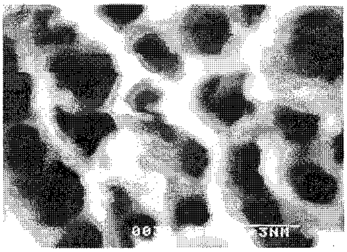

Figure 1. SEM picture of dried PVF_2- camphor gel (W_{PVF_2} =0.25).

For thermodynamic study the gels were prepared in Perkin Elmer large volume capsules (LVC) by taking appropriate amount of polymer and camphor and the capsules were tightly sealed with help of a quick press. The samples were subsequently made homogeneous by keeping at 200 ^{0}C in DSC for 15 min with occasional shaking, and then were gelled at –30 ^{0}C for 10 min by cooling from 200 ^{0}C at the rate of 200 ^{0}C / min. They were then heated at the scan rate of 40 ^{0}C/min, the higher heating rate was chosen to avoid recrystallization processes. The enthalpies and melting temperatures were determined by means of a computer attached to the instrument.

Result and discussion

In Fig-1 the SEM picture of dried PVF_2/camphor gel ($W_{PVF_2} = 0.25$) is shown. From the figure fibrillar network structures are clearly observed. The heating thermograms (Fig- 2) of the gel exhibit *first order* phase transitions. Thus the presence of fibrillar network structure and first order phase transitions indicate formation of thermoreversible gel [2]. In figure 3 are presented the temperature-concentration phase diagram as obtained from the maxima of the 1st order transitions together with the Tamman's diagram (enthalpies vs concentration). Two non-variant temperature events can be observed at T= 135°C and T= 150°C. Also, one observes that the 1st order transition in the camphor-reach systems occur at temperatures higher than the pure camphor melting point. We conclude that the 1st order transition is connected to a liquid-liquid phase separation.

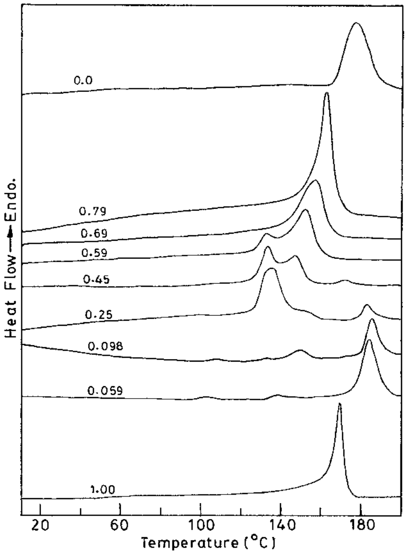

Figure 2. DSC traces obtained at 40°C/mn for variation PVF_2/camphor compositions (as indicated).

Applying GIBBS rules for establishing the phase diagram, we conclude that the first non-variant event corresponds to the incongruent-melting of a compound (C_I) while the second one corresponds to the formation of an eutectic between a camphor solid solution (S_c) and pure PVF_2. Note that the composition of the camphor solid solution (S_c) varies with temperature. It contains little PVF_2 at low temperature but more as temperature is increased. The variation of the enthalpies are consistent with the present description of the phase diagram. Note that in the PVF_2-rich systems, the enthalpies associated with the liquidus line do not vary linearly as they should. This arise from the fact that the maximum at 150°C representing the eutectic melting event cannot be properly extracted from the DSC traces. If we consider that the enthalpy associated with the liquidus should vary linearly (dotted line) then we can calculate what should be the values for the enthalpy of the non-variant event at 150°C. These values do fall on the dashed line expected for the variation of the enthalpies associated with the eutectic melting.

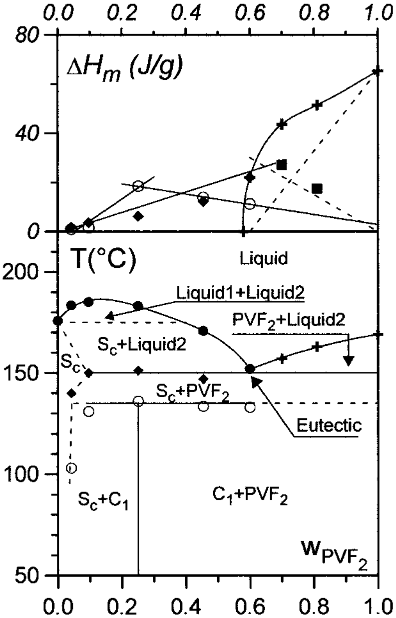

Figure 3. Phase diagram of PVF_2/camphor systems obtained from DSC melting endotherms. As is customary, the dotted lines stand for event that are not explicitly observed, but that should exist on the basis of GIBBS phase rules.

From the maximum at $W_{PVF_2} = 0.25$ of the enthalpy associated with the event at T= 135°C (incongruent-melting of the compound) we deduced a stoichiometric composition for C_I of *4 PVF_2 monomer unit/5 camphor molecules.*

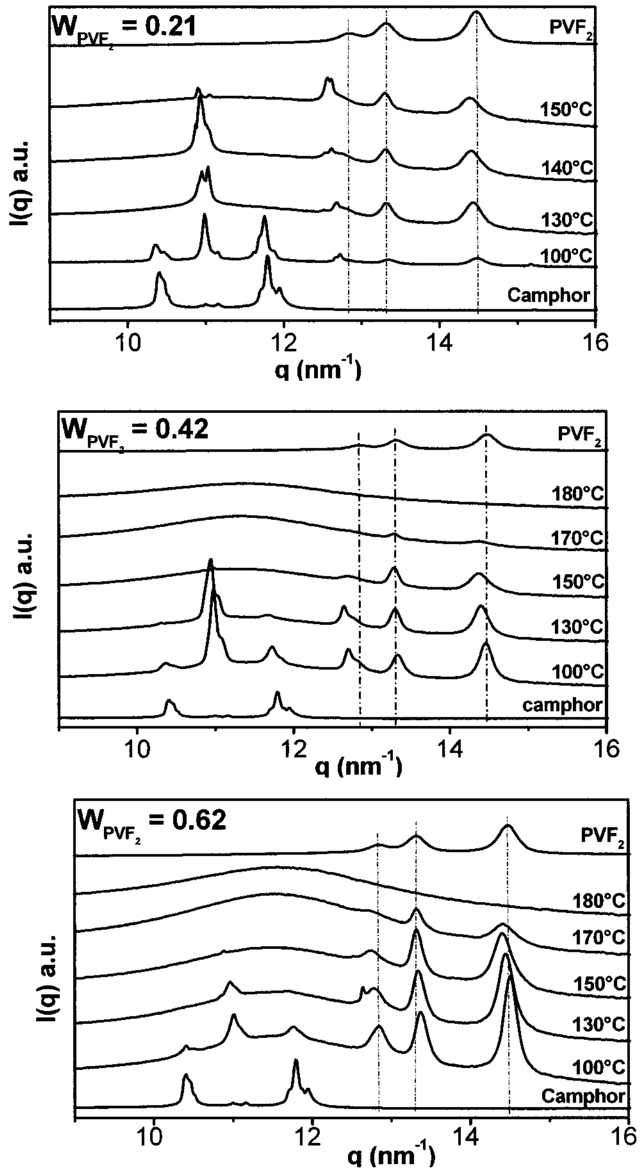

Figure 4. Time-resolved synchroton X-ray diffractograms for *PVF_2/camphor* systems. Compositions and temperatures as indicated. Dotted lines show the position of the reflections for pure PVF_2. Here, the heating rate was about 2°C/mn.

Time-resolved X ray patterns for some of PVF_2 /camphor compositions are shown in Fig-4. together with the diffractograms at 20^0C of pure camphor and pure PVF_2.

Some noticeable alterations of the X-ray patterns have occurred compared to the linear combination of the components diffractograms. Note that a shift of the transitions is expected with respect to those reported on phase diagram because this latter is drawn on the basis of the maxima of the endotherms while the X-rays patterns, particularly the disappearance of reflections, are linked to the end of the endotherm.

In the three spectra shown in figure 4 one can observe a strong reflection at $q\approx$ 11 nm^{-1} which disappears above 140°C. It does not correspond to any of the reflections of either pure camphor nor pure PVF_2. We suggest that this peak stands for the crystalline lattice of compound C_1. The solid solution S_c is most probably characterized by the peaks at $q\approx12.6$ nm^{-1}, together with those of pure PVF_2. It is likely that this phase consists of camphor crystals alternating with PVF_2 crystals in a way already described by Wittmann and St John Manley [8]. It is also worth emphasizing that the composition of the solid phase S_c is temperature-dependant. Below 135°C, camphor crystals are probably large enough so as to give the camphor reflections at 10.4 and 11.9 nm^{-1}. While above 135°C, the situation changes, hence the disappearance of these reflections.

Conclusion

PVF_2 produces thermoreversible gels with camphor having fibrillar network morphology and reversible first order phase transition. Evidence for a polymer-solvent compound in this gel has been put forward from both thermodynamic study and synchroton X-ray study of the samples.

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