Phase separation in mixtures of poly(vinylidene fluoride) and hydroxypropyl cellulose

S. Ambrosino and P. Sixou*
Physique de la Matière Condensée, UA 190 CNRS, Parc Valrose, 06034 Nice Cédex, France

(Received 12 March 1990; revised 21 February 1991; accepted 25 February 1991)

Phase separation has been studied in a mixture composed of a crystalline polymer, poly(vinylidene fluoride) (PVDF), and a mesomorphic polymer, hydroxypropyl cellulose (HPC). The mixture was first studied in solution in a common solvent of the two polymers: the ternary phase diagrams showed a large incompatibility between the two polymers with different chemical structures. Then the solvent was evaporated, and phase separation was studied in the resulting solid biphasic films. The determination of binary phase diagrams as a function of temperature revealed that each phase was composed mainly of one polymer. We also studied the influence of various parameters on the size of the droplets in these films: the proportions of the two polymers (the size of the droplets was larger when the two polymers were in equal proportions, and decreased when the quantity of polymer in the droplets decreased), the polymer concentration in the initial ternary solutions (the size of the droplets increased with polymer concentration), the evaporation rate of the solvent (the size of the droplets in the solid films decreased when the evaporation rate was increased) and the molecular weight of PVDF (the size of the droplets decreased when the molecular weight of PVDF was increased). We have tried to explain the variations observed using ternary phase diagrams, Binder's theory concerning mixtures of two polymers in the melt and by macromolecular diffusion phenomena.

(Keywords: phase separation; mixtures; poly(vinylidene fluoride); hydroxypropyl cellulose)

INTRODUCTION

In recent years, increasing attention has been devoted to polymer mixtures. Mixing polymers is easier and cheaper than synthesizing new molecules, and the resulting mixtures exhibit properties of the component polymers. However, the main difficulty encountered in the preparation of mixtures is the quasi general immiscibility of polymers with different chemical structures. Thus it is necessary to study the phenomenon of phase separation from a fundamental point of view, why it must be eliminated in some cases, slowed down in others and taken advantage of in still others. Several theories[1–5] deal with polymer mixtures and try to predict phase diagrams for binary or ternary mixtures of rigid, semi-rigid or flexible chain polymers.

In our experiments, we have studied phase separation in a mixture of two incompatible polymers: hydroxypropyl cellulose (HPC) and poly(vinylidene fluoride) (PVDF). Individually, each polymer exhibits interesting properties.

HPC is a mesomorphic polymer with cholesteric mesophases. It is thermotropic between ~160°C and 200°C depending on the molecular weight, and gives lyotropic phases in various solvents. Its birefringence is responsible for interesting optical properties.

Interest in PVDF has grown over the last few years because of its processability, mechanical strength and chemical resistance. It may also exhibit ferroelectric properties. The crystalline phase of PVDF (birefringent spherulites), responsible for some properties of the polymer, has been extensively studied[6]. PVDF may exhibit various crystalline phases (α, β, γ or δ), according to the conformation of the chains and their molecular packing at different temperatures. The resulting phase depends on the experimental process[6]. PVDF is among the very few crystalline polymers that is thermodynamically compatible with other polymers such as poly(alkyl methacrylates), a few poly(alkyl acrylates), poly(vinyl acetate) and poly(vinyl methylacetone)[7–11]. In these cases, compatibility has been monitored through variations in the glass transition temperature (T_g) and the drop in the melting point of the crystalline polymer.

Phase separation in HPC–PVDF mixtures will be discussed elsewhere in a study of the kinetics of crystallization of PVDF in the same incompatible mixtures.

EXPERIMENTAL

The HPC was obtained from Hercules (Klucel E) and had a weight-average molecular weight of 60000 g mol^{-1}.

The PVDF was a Kynar grade obtained from Penwalt Ltd. Two molecular weights were studied: Kynar 721 ($M_w = 45000$, melting point 170°C); Kynar 301 ($M_w = 350000$, melting point 155–160°C).

---

* To whom correspondence should be addressed

0032-3861/92/040795-06

N,*N*-dimethylacetamide (DMAC) was obtained from Aldrich and used as solvent.

The solutions of HPC/PVDF/DMAC were made by dissolving the two polymers in the solvent, followed by vigorous stirring. The studies were made 24 h after preparing the samples. Solid films were produced by evaporating the solvent. The solutions were stirred and spread on a glass slide with a 'hand-coater', which allowed the thickness of the solutions to be regulated.

The solutions studied were 100 μm thick, which resulted in solid films 10–20 μm thick after evaporation of DMAC. The solvent was evaporated by depositing the glass slides on a hot-plate at 50°C for ~30 min. The resulting solid films were crystallized to 20°C above the melting point of PVDF (190°C for Kynar 721 and 180°C for Kynar 301) and annealed for 30 min. The films were rapidly cooled to the isothermal crystallization temperature.

The ternary phase diagrams of HPC/PVDF/DMAC were determined at room temperature and phase diagrams of HPC/PVDF as a function of temperature (on solid films) were studied using an Olympus polarizing microscope BHSP equipped with a Mettler hot stage FP52. The size of the droplets in the biphasic films was determined by studying the photographs obtained.

RESULTS AND DISCUSSION

Ternary phase diagrams at room temperature

The compatibility of HPC and PVDF was studied in a common solvent (DMAC) as the samples degraded when prepared in the melt. Phase separation in HPC/PVDF mixtures was then studied in solid films composed of the two polymers, obtained, as discussed above, by evaporating the solvent.

Figure 1 shows the ternary phase diagrams of HPC/PVDF/DMAC at room temperature. In these diagrams we note:

- there are three main regions: isotropic, isotropic–isotropic and isotropic–anisotropic;
- that only a part of the phase diagrams, corresponding to diluted solutions, has been determined due to a sharp increase in the viscosity of the solutions with polymer concentration, particularly mixtures pertaining to PVDF;
- that just enough points of the phase diagram obtained with PVDF K301 have been plotted in order to compare it to the phase diagram of the mixture containing PVDF K721;
- that in both cases (PVDF K721 and K301) compatibility is very low since phase separation occurs in solutions with polymer concentrations of <10%;
- that in both diagrams, the limits of the isotropic–biphasic isotropic phase separation are virtually identical even though the two grades of PVDF (K721 and K301) have different molecular weights (45 000 and 350 000, respectively).

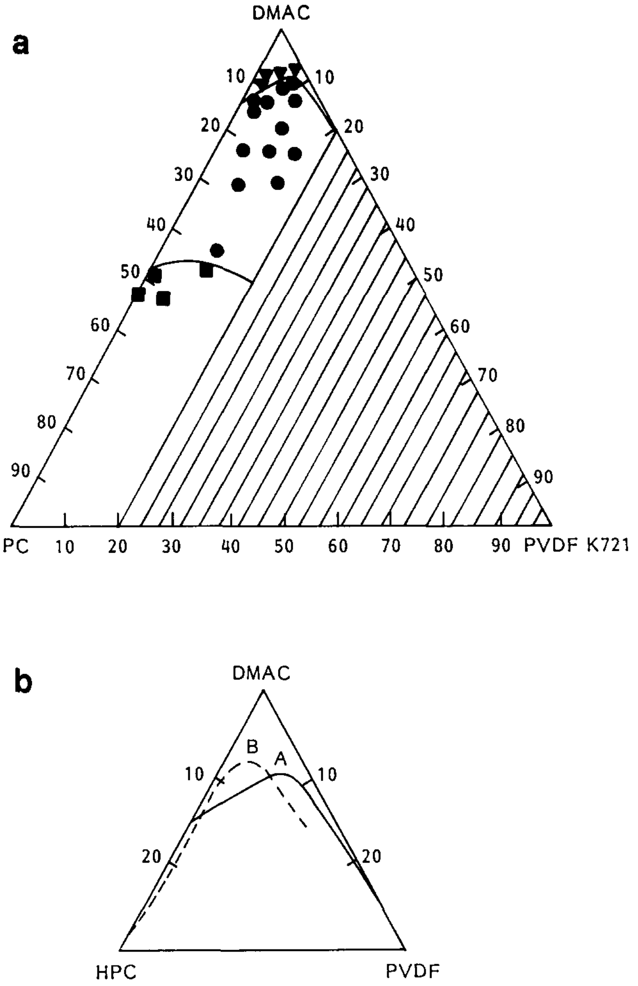

Figure 1 Ternary phase diagrams HPC/PVDF/DMAC at room temperature. (a) HPC/PVDF K721/DMAC: (▼) isotropic; (●) isotropic–isotropic; (■) anisotropic. (b) Comparison of the limits of phase separation between PVDF K721 (A) and PVDF K301 (B)

Phase diagrams of HPC/PVDF as a function of temperature

The films obtained through the heat treatment described earlier are used in several ways to study the phase diagram of HPC/PVDF as a function of temperature, and also to study the variation in the size of the droplets in the biphasic films as a function of different parameters such as proportions of HPC and PVDF, initial polymer concentration in DMAC, solvent evaporation conditions, and molecular weight of PVDF. *Table 1* lists: the proportions of the two polymers; the polymer concentration in the initial solution (in parentheses); T_{t_1} which is the melting point of PVDF (K721 and K301) alone or in mixtures, and T_{T_2} which is the anisotropic–isotropic transition temperature of HPC alone or in mixtures; and the results obtained using the two grades of PVDF.

The corresponding phase diagrams are plotted in *Figure 2* for PVDF K721 (*Figure 2a*) and PVDF K301 (*Figure 2b*). Points correspond to the average values of different measurements at each concentration. The transition temperatures of mixtures of HPC and PVDF (K721 and K301) remain essentially unchanged compared to those of the individual polymers. This indicates that each phase of the mixture is composed mainly of one polymer.

Variation in size of the droplets in HPC/PVDF solid films

The variation in size of the droplets in the biphasic films was studied as a function of various parameters. (Some of the parameters are relative to the initial solutions HPC/PVDF/DMAC, so it may be helpful to refer to the ternary phase diagrams.)

Table 1 Transition temperatures of PVDF and HPC on heating and on cooling for various concentrations

PVDF	HPC/PVDF proportions[a]	$T_{t_1}\uparrow^b$ (°C)	$T_{t_2}\uparrow^b$ (°C)	$T_{t_1}\downarrow^c$ (°C)	$T_{t_2}\downarrow^c$ (°C)
K721	100/0	–	197	–	–
	82/18 (17)	168	195	(135)	190
		167	196	133	(182)
	78/22 (45)	170	198	144	192
		170	195	144	(184)
	75/25 (15–20)	170	195	142	190
		169	195	143	186
	75/25 (10)	170	197	147	193
	75/25 (5)	169	196	142	191
		170	196	138	188
	50/50 (10)	170	198	146	191
	43/57 (diluted)	170	198	143	–
		169	–	–	157
	25/75 (5)	170	200	142	192
		168	–	–	190
	25/75 (10)	173	196	147	–
	0/100	170	–	147	–
K301	100/0	–	197	–	–
	75/25 (10)	160	199	140	189
	50/50 (10)	161	198	139	181
	25/75 (10)	161	–	139	–
	0/100	160	–	144	–

[a] Concentration (%) of polymer in the solvent in parentheses
[b] Transition observed during heating
[c] Transition observed during cooling

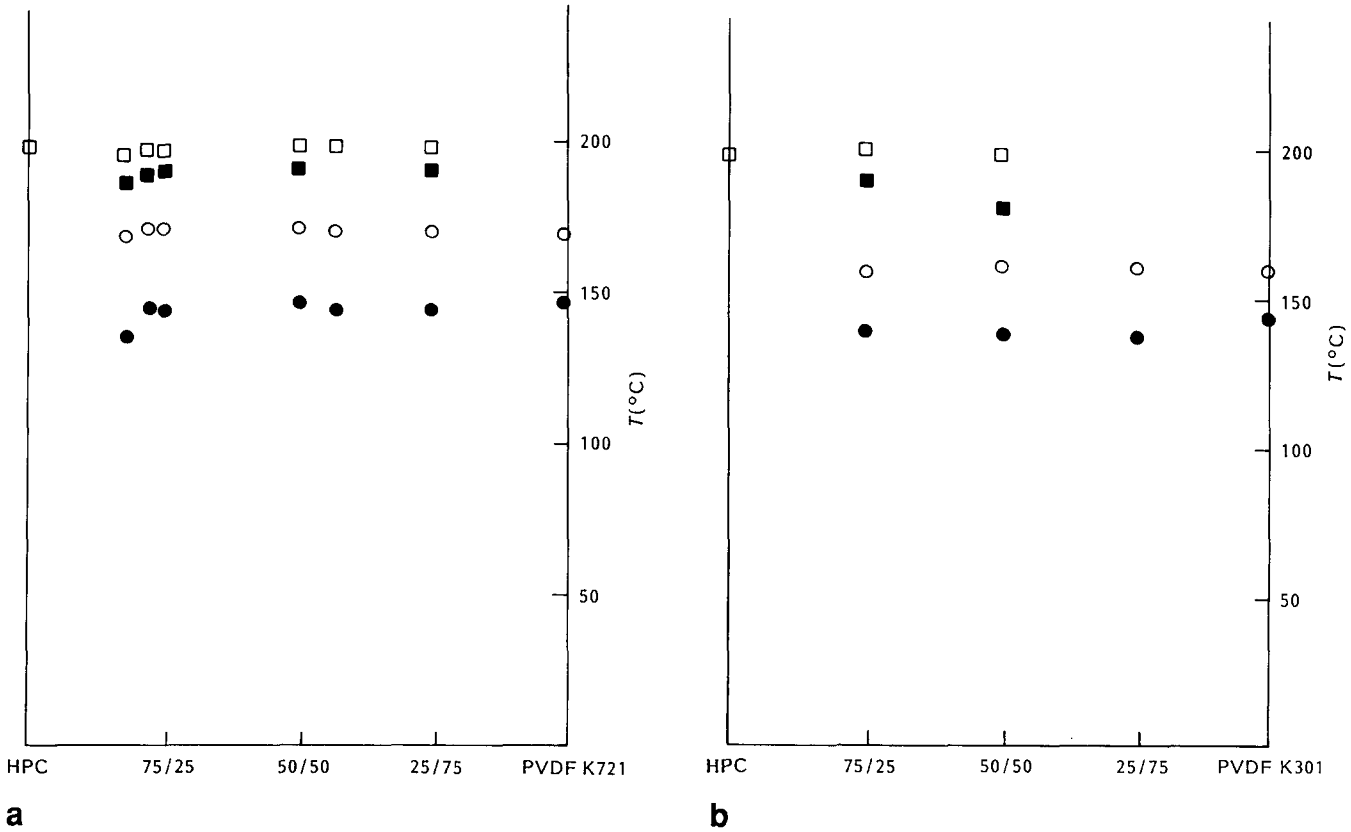

Figure 2 Phase diagrams of HPC/PVDF mixtures (solid films obtained by evaporating the solvent) as a function of temperature: (a) HPC/PVDF K721; (b) HPC/PVDF K301. Transition HPC: (□) during heating; (■) during cooling. Transition PVDF: (○) during heating; (●) during cooling

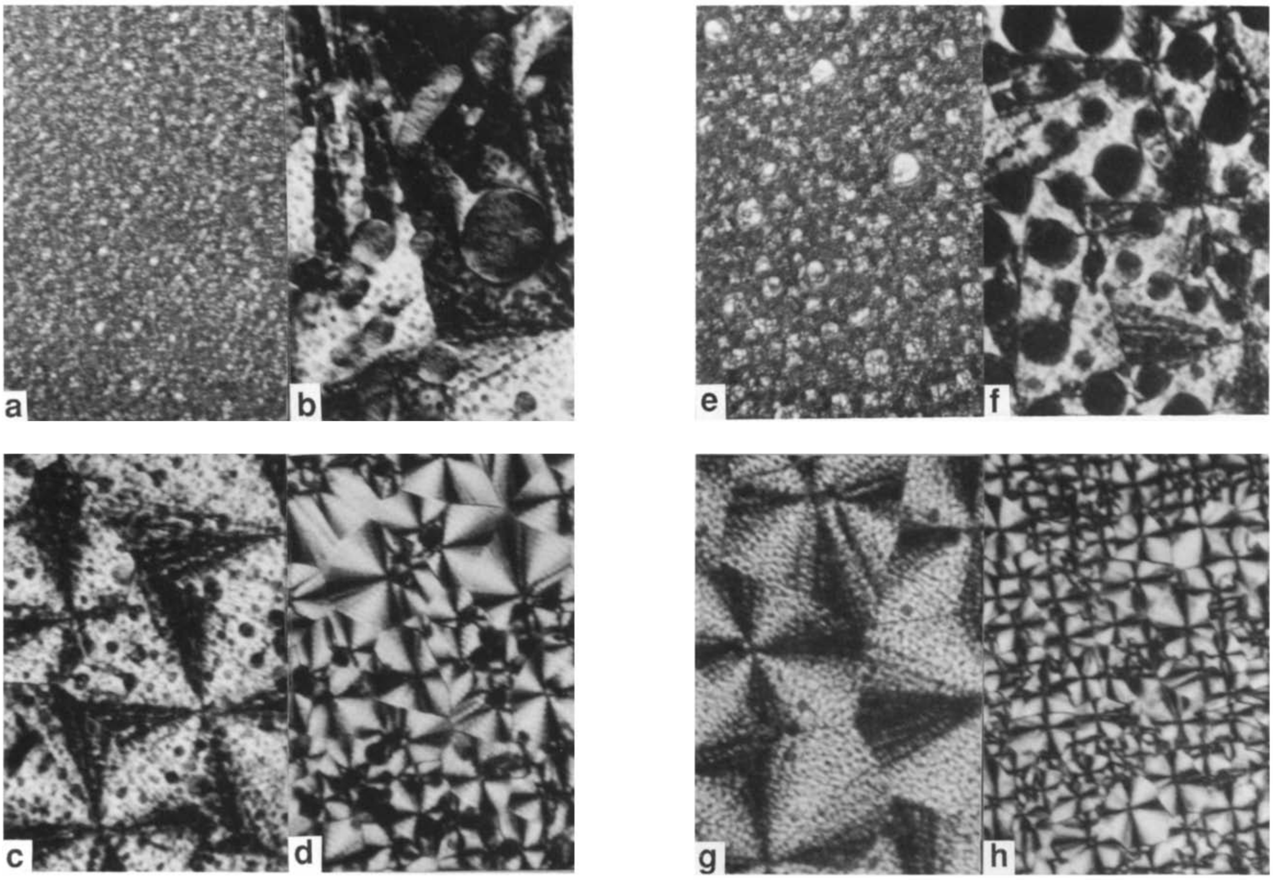

Figure 3 Microphotographs of HPC/PVDF solid films with different HPC/PVDF proportions (K721 and K301), magnification ×413: (a) HPC/PVDF K721 = 75/25; (b) HPC/PVDF K721 = 50/50; (c) HPC/PVDF K721 = 25/75; (d) HPC/PVDF K721 = 0/100; (e) HPC/PVDF K301 = 75/25; (f) HPC/PVDF K301 = 50/50; (g) HPC/PVDF K301 = 25/75; (h) HPC/PVDF K301 = 0/100

Variation as a function of HPC/PVDF proportions. Solid films prepared as described earlier were used. In the thermal treatment, the crystallization temperatures were 155 and 145°C for HPC/PVDF mixtures containing PVDF K721 and PVDF K301, respectively. *Figure 3* shows the micrographs of the solid films obtained with the two grades of PVDF and for different proportions of the two polymers. *Figures 3d* and *h* show the typical texture of PVDF of birefringent spherulites. Note that in mixtures, the phase based on the crystalline texture of PVDF can be identified. We have also examined droplets of PVDF in the HPC matrix in mixtures composed mainly of HPC, and droplets of HPC in the PVDF matrix in mixtures composed mainly of PVDF or in equal proportions with HPC. When there was more PVDF, the size of the droplets of HPC increased with the amount of HPC*. However, as can be seen in *Figure 3*, the size of the droplets reaches a maximum with equal proportions of the two polymers, and then decreases when the quantity of the polymer in the droplets decreases.

We have tried to explain this variation in the size of droplets as a function of HPC/PVDF proportions using ternary phase diagrams at room temperature (*Figure 1*).

Very dilute solutions (polymer concentrations of 5, 10 and 15%) were used to prepare solid films, i.e. isotropic or isotropic–isotropic.

For initial homogeneous (isotropic) solutions, solvent evaporation led to the solutions being concentrated and phase separation occurred (for a polymer concentration of ~10%) by the nucleation and growth mechanism. There was also coalescence in the droplets if the viscosity was sufficiently low.

Binder's theory[12] predicts for mixtures of two polymers in the melt:

- variation, for nucleation, of the critical radius of nuclei (R^*) as a function of the proportions of the two polymers (*Figure 4*);
- linear growth of the droplets;
- coalescence in the droplets if the viscosity is sufficiently low.

However, since Binder predictions involve a temperature dependence on phase separation, comparison to our experiment is only qualitative.

The variation in size of the droplets as a function of HPC/PVDF proportions in solid films (and thus in biphasic solutions of identical polymer concentrations during solvent evaporation) is the reverse of R^* proposed by Binder (cf. *Figures 3* and *4*). Thus, to explain our experimental results, the factor determining the final size of droplets in biphasic films is most likely the rate of growth of droplets in solutions during solvent evaporation, this rate being proportional to the final size of the droplets.

Growth continues in solutions during solvent evaporation (with an increase in polymer concentration) until

---

* Only one case has been studied in which there was more HPC, i.e. when PVDF was contained in droplets, so a full comparison could not be made

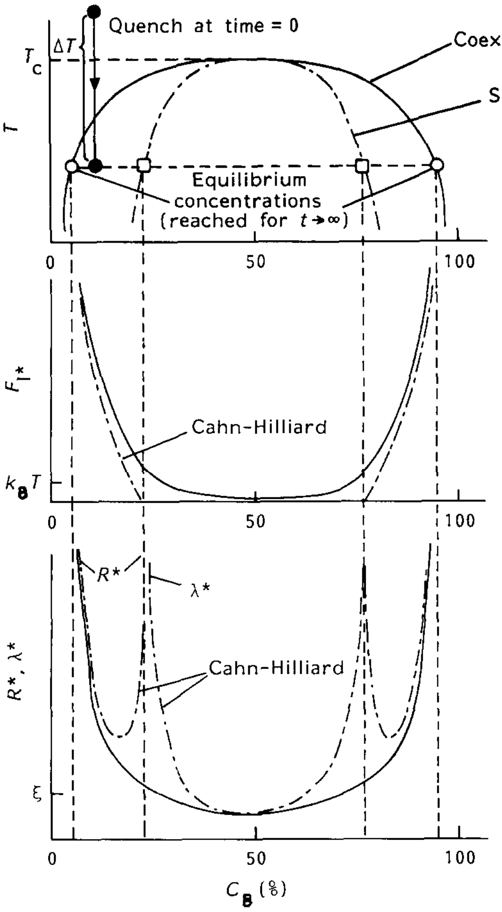

Figure 4 Phase separation in a mixture of two polymers. Variation in the critical size of droplets as a function of the concentration in the two polymers (adapted from ref. 12)

the gel region is reached, i.e. the viscosity of the solutions is so high that the systems are considered to be solid.

If the initial solutions are biphasic (polymer concentration of $>10\%$), only the growth of droplets (no nucleation) may be taken into account and, as was previously the case, it may be supposed that the rate of growth of droplets is proportional to the final size of the droplets.

Variation as a function of the initial polymer concentration in DMAC. The influence of the initial solution polymer concentration on the size of the droplets in solid films using PVDF K721 was examined. We observed that the size of droplets increased with the initial polymer concentration.

Binder's theory[13] for mixtures of two polymers in the melt predicts a decrease of R^* when $\Delta T = (T_{\text{critical}} - T)$ is increased. Recall that the growth rate of droplets is linear. We assume once again that the variation in temperature for this kind of system corresponds to a variation in solution mixture concentration. The variation in the size of droplets as a function of polymer concentration in our systems is therefore the opposite of that for R^* as predicted by Binder.

Thus, as discussed earlier, the factor governing the variation observed is probably the growth rate of droplets in solution. Larger droplets are obtained in solid films for high polymer concentrations in the initial solutions, all other conditions being equal.

The variation in the size of droplets in biphasic films with HPC/PVDF proportions and with the initial polymer concentration can be explained in the same way. As the variation in R^* is the opposite of that for the size of droplets in HPC/PVDF films, it may be supposed that the factor governing the variation observed is the growth rate of droplets.

Variation with the evaporation rate of solvent. This study was conducted with mixtures of HPC and PVDF K721. We observed that the size of droplets in solid films obtained after solvent evaporation decreased with increase in the evaporation rate of DMAC.

Polymer concentration was low in the initial solutions (between 5% and 15%), and the solutions were either isotropic or isotropic–isotropic. During solvent evaporation, polymer concentration increased, nucleation and growth occurred in the monophasic solutions when the limit of phase separation was reached (*Figure 1*), whereas only droplet growth occurred in biphasic solutions. This phenomenon stopped when the gel region was reached, and there was no further modification to the systems until the end of evaporation. When evaporated rapidly, the gel region was quickly reached, and droplets had no time to grow, which explains why they were small in solid films. It followed that droplets were larger with a slower evaporation rate.

Variation with the molecular weight of PVDF. The size of droplets in films containing PVDF K721 ($M_w = 45000$) was compared with those in films containing PVDF K301 ($M_w = 350000$), with constant HPC/PVDF proportions, identical initial polymer concentration and the same solvent evaporation conditions, except for HPC/PVDF = 75/25 (*Figure 3*). We observed that the size of the droplets decreased when the molecular weight of PVDF increased. We explained this by the fact that for the higher molecular weight, diffusion of macromolecules was slower in solutions during solvent evaporation, and consequently droplets grew more slowly and hence were smaller in the resulting solid films.

CONCLUSIONS

HPC/PVDF mixtures studied in this work follow the general rule of incompatibility of polymer mixtures, as demonstrated by phase diagrams. We have also shown that the size of droplets in biphasic solid films composed of HPC and PVDF, produced by evaporating the solvent from HPC/PVDF/DMAC solutions, can be varied with several parameters, including proportions of the two polymers and polymer concentration in the initial solutions. The preparation of the solid films, particularly solvent evaporation, also plays an important role in the final droplet size. Finally, this mixture was easy to study due to the characteristic textures of the two polymers.

REFERENCES

1 Champetier, G. and Monnerie, L. 'Introduction à la Chimie Macromoléculaire', Masson, Paris, 1969, Ch. 2, pp. 107–128
2 Brochard, F., Jouffroy, J. and Levinson, P. *J. Phys.* 1984, **45**, 1125

3 Ten Bosch, A. and Maïssa, P. 'Lecture Note in Physics 268; Fluctuations and Stochastic Phenomena in Condensed Matter', Springer-Verlag, Berlin, 1987, pp. 333–350

4 Ten Bosch, A., Pinton, J. F., Maïssa, P. and Sixou, P. *J. Phys.* 1987, **A20**, 4531

5 Flory, P. J. *Macromolecules* 1978, **11**, 1138

6 Lovinger, A. J. in 'Developments in Crystalline Polymers' (Ed. D. C. Basset), Vol. 1, Applied Science, London, 1982, Ch. 5

7 Kwei, T. K., Patterson, G. D. and Wang, T. T. *Macromolecules* 1976, **9**, 780

8 Wendorff, J. H. *J. Polym. Sci., Polym. Lett. Edn* 1980, **18**, 439

9 Nishi, T. and Wang, T. T. *Macromolecules* 1975, **8**, 909

10 Saito, H., Fujita, Y. and Inoue, T. *Polym. J.* 1987, **19**, 405

11 Reckinger, C. and Rault, J. *Rev. Phys. Appl.* 1986, **21**, 11

12 Binder, K., Billotet, C. and Mirold, P. *Z. Physik.* 1978, **B30**, 183

13 Binder, K. *J. Chem. Phys.* 1983, **79**, 6387