Alcohol–water cosolvent systems for poly(methyl methacrylate)

John M. G. Cowie, Mahmood A. Mohsin and Iain J. McEwen
Department of Chemistry, University of Stirling, Stirling FK9 4LA, UK

(Received 2 February 1987; accepted 9 March 1987)

Mixtures of water and alcohols, containing up to 0.4 volume fraction water, have been found to dissolve poly(methyl methacrylate). Phase boundaries have been established and these indicate significant cosolvent action. Cosolvency in water–2-propanol mixtures is confirmed by viscosity measurements. A possible mechanism for cosolvency is discussed.

(Keywords: cosolvent mixture; water; alcohol; poly(methyl methacrylate))

INTRODUCTION

In general, the lower aliphatic alcohols are regarded as non-solvents for poly(methyl methacrylate) (PMMA). However, at slightly elevated temperatures this is no longer the case and it has been shown that methanol and ethanol are solvents at ca. 360 K and above[1]. Water, on the other hand, has essentially no affinity for PMMA whatsoever and may be regarded as an absolute non-solvent.

PMMA is used as a polymeric electron beam resist which is normally developed using a solvent such as methyl ethyl ketone. However, it has been observed that 2-propanol, containing a few per cent water, was capable of dissolving low molecular weight material resulting from the irradiation of high molecular weight PMMA[2]. In order to obtain a clearer picture of this effect it was decided to study the phase behaviour of PMMA in mixtures of water with water-miscible alcohols to establish both the temperature and the solvent composition limits of solubility.

As described previously[3–6], polymer–solvent phase diagrams are a convenient means of characterizing the solvating power of a mixed solvent. Two phase separation temperatures are normally found in polymer solutions, i.e. the upper and the lower critical solution temperatures (UCST and LCST). The former is primarily enthalpic in origin, occurring as the temperature is lowered and as the polymer–solvent interactions become insufficiently favourable for solution. The LCST occurs at elevated temperatures and is primarily an entropic effect arising from the differences in free volume between highly expanded solvent and the polymer. Enhanced polymer solvation, as by a cosolvent mixture, is evidenced by an increased interval between UCST and LCST[3–6].

EXPERIMENTAL

A BDH PMMA sample was characterized in this laboratory, yielding M_n 48×10^3 g mol^{-1} with $M_w/M_n \simeq 1.8$. The other samples used have been characterized previously[7]. All samples were essentially atactic.

The alcohols were normal reagent grade and were used without further purification. Distilled water–alcohol mixtures were made up by volume.

The phase separation temperatures were established for dilute polymer solutions (3% wt/vol) in thick-walled Pyrex tubes as previously described[3–6].

The viscosity of PMMA in 2-propanol–water mixtures was determined in an Ubbelohde viscometer at 303 K.

RESULTS

The UCST phase behaviour of PMMA (48×10^3) in mixtures of methanol, ethanol, 1-propanol, 2-propanol and 2-methyl-2-propanol (t-butanol) with water is shown in *Figure 1.* The alcohols are themselves solvents at temperatures which decrease with increasing size of the alkyl group. Beyond volume fraction ca. 0.5 the mixtures are essentially non-solvents, but around volume fraction 0.8 enhanced solvation is evident and both 1- and 2-propanol–water mixtures will dissolve PMMA at room temperature. Similar behaviour is shown by t-butanol, although the composition range is more restricted.

Water–propanol is reported to dissolve poly(ethylene glycol monomethacrylate)[8] but here there is an understandable interaction between this polymer and both solvents. 2-Propanol is a theta solvent for poly(ethyl methacrylate) and light scattering and viscometric studies of this polymer in aqueous 2-propanol indicate that the addition of water actually brings about better solvation of the polymer coil[9]. Here it is confirmed, rather surprisingly, that synergism occurs to provide a solvent medium considerably better for PMMA than either the alcohol or, even more dramatically, water alone.

Figure 2 shows the behaviour of PMMA in 2-propanol–water for a number of molecular weights. For PMMA 830×10^3 and 439×10^3, phase separation under LCST conditions was also observed. For the latter molecular weight, some evidence of thermal degradation was observed since on recooling the samples the original UCST phase separation could not be reproduced. Nevertheless, the resulting phase diagram has a form similar to previously established 'pseudo-classical' cosolvent systems[5,6]. The cosolvent action of the mixture 2-propanol–water is confirmed by the plot of intrinsic viscosity vs. solvent composition in *Figure 3.* Maximum coil expansion occurs at volume fraction 0.8, corresponding to the composition of the maximum miscibility gap in *Figure 2.*

0032–3861/87/091569–04$03.00

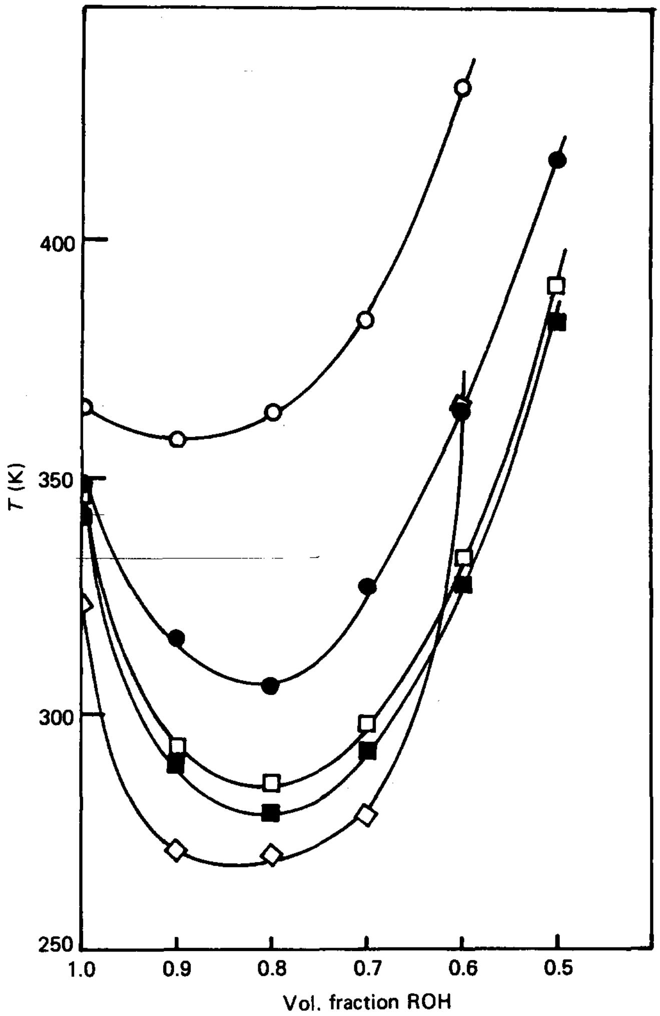

Figure 1 Demixing temperatures for 3% wt/vol solutions of PMMA 48×10^3 g mol^{-1} in water–alcohol mixtures as a function of the volume fraction alcohol. ○, Methanol; ●, ethanol; □, 1-propanol; ■, 2-propanol; ◇, t-butanol

Although the phase contours of *Figure 1* could not be completed, comparison of 2-propanol–water with the other mixtures indicates that cosolvent action is present in all cases, although with methanol–water this is likely to be minimal. It is intriguing to contrast this latter mixture with the methanol–cyclohexane system (the combination of alcohol with non-polar alkane) which also exhibits a cosolvent action for PMMA[1].

DISCUSSION

Cosolvency results from enhanced solvation of a polymer chain compared with that in the component single solvents. This may be observed by determining the coil size or the increased separation of UCST and LCST. As mentioned in the introduction, the former demixing type results from enthalpic effects and the latter from entropic (free volume) effects. The Paterson–Prigogine–Flory theory of polymer solutions embodies both of these through equation (1), which predicts the phase separation temperature (T) as a function of polymer (component 2) chain length (r).

$$\frac{T_1^* c_1 \nu^2}{T\tilde{V}_1} + \frac{c_1 \tau^2}{2(\frac{4}{3}\tilde{V}_1^{-1/3} - 1)} = \frac{(1 + r^{-1/2})^2}{2} \qquad (1)$$

The parameter $c_1 \nu^2$ characterizes polymer–solvent interactions and $c_1 \tau^2 = c_1(1 - T_1^*/T_2^*)^2$ quantifies free volume.

T^* is the temperature reduction parameter and $\tilde{V}_1$ is the reduced volume of the solvent or mixed solvent (component 1). The application of this equation to mixed solvents and the derivation of the necessary equation of state parameters has been fully described before[3–6].

In general, it has been concluded from these previous studies that cosolvency occurs when the components of the mixture can preferentially (and separately) solvate different sites on the polymer chain. To fulfil this requirement, the molecular characteristics of the components have to differ somewhat in terms of polarity, size and shape. The free volume of such mixtures may be calculated from the heat of mixing (H^E), and the consequence of molecular disparity (endothermic H^E)

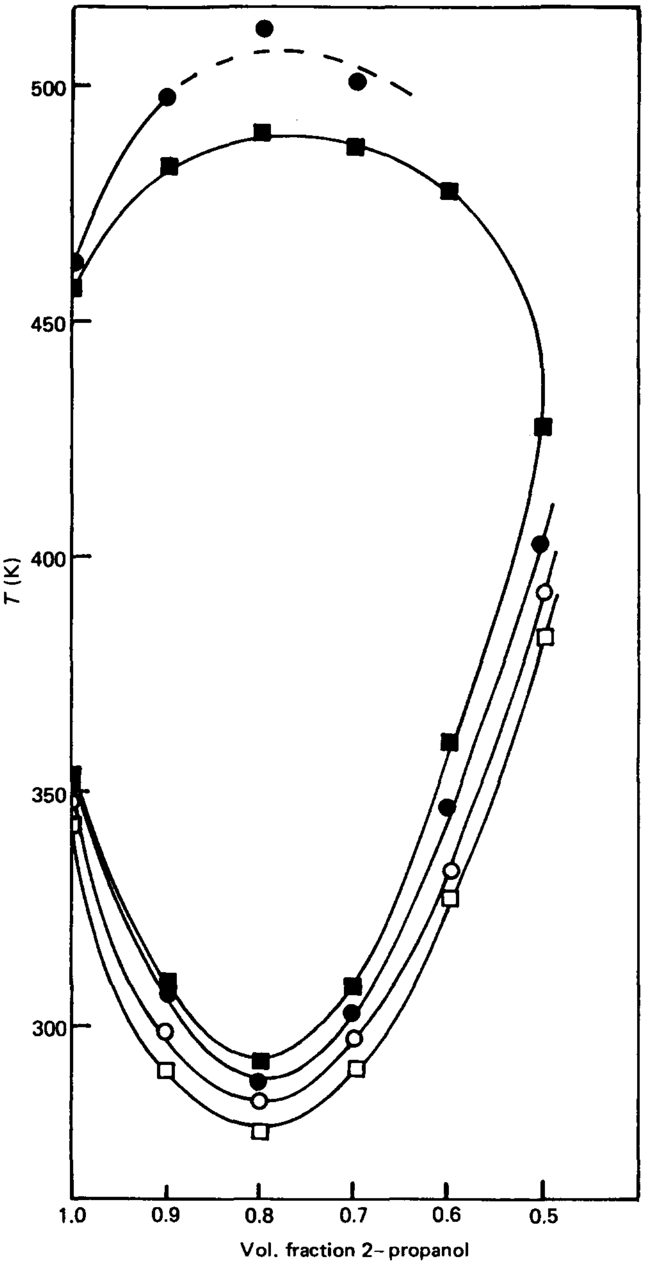

Figure 2 Demixing temperatures for 3% wt/vol solutions of PMMA in 2-propanol–water. PMMA molecular weight $\times 10^3$ g mol^{-1}: □, 48; ○, 337; ●, 439; ■, 830

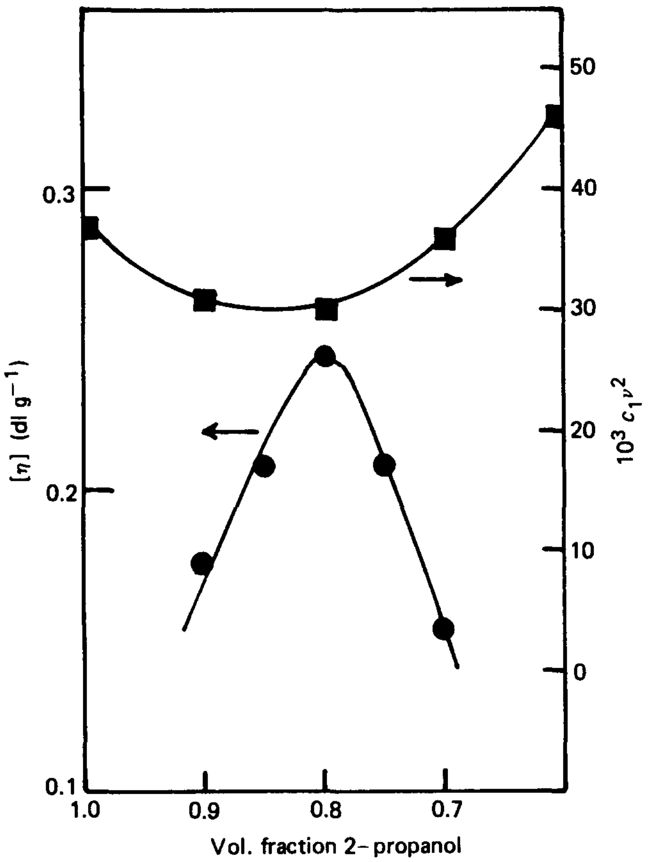

Figure 3 Variation of the intrinsic viscosity (●) of PMMA 48×10^3 g mol^{-1} and of the interaction parameter c_1v^2 in water–2-propanol (■)

results in a free volume contribution which is opposed to cosolvent action. Cosolvency results consequently from enthalpic effects which are reflected by the c_1v^2, composition behaviour in polymer–mixed solvent systems[5,6].

The foregoing conclusions, and the models which form the basis of (1), apply to systems exhibiting only van der Waals or dispersive-type interactions. In the present mixtures, strong specific forces are present in the form of H-bonds between the solvent components. Nevertheless, it is reasonable to assume that the same balance of enthalpic and entropic effects is present in such systems, and it is possible to examine the latter directly from literature values of the expansion coefficients for water–methanol[10] and water–2-propanol[11]. *Figure 4* shows the variation of T_1^* for these two combinations calculated as before[5,6]. The 'negative' deviation suggests that the mixtures are more expanded than would be the case if linear behaviour pertained. In free volume terms they are poorer than a linear average, and the observed cosolvent effect of the mixtures must lie elsewhere.

Water–alcohol mixtures have been extensively reviewed[12] and the role of hydrogen bonding is seen in the sign of H^E; for methanol–water and ethanol–water, H^E is negative but, as the alkyl chain lengthens, H^E becomes positive for alcohol-rich compositions[13,14]. For example, although mixing of 1-propanol and water at compositions below 0.3 mol fraction is exothermal, this is reversed above 0.3 mol fraction. In this latter composition range non-specific (physical) interactions predominate over specific (chemical) H-bonding effects. According to McGlashan[15] and to Goodwin and Newsham[14] physical interactions should not be neglected. For example, the equimolar enthalpy of mixing for a classic cosolvent system for polystyrene, acetone + hexane[16], (where no specific interactions can be envisaged) is $+1560$ J mol^{-1}, actually larger than the heats of mixing of alcohols with water. Thus it may be assumed that relatively large physical interactions, as well as H-bonding, contribute to the properties of alcohol–water mixtures and that the measured values of H^E are an aggregate of an exothermal H-bonding component and an endothermic physical component.

The change of H^E with temperature for the ethanol–water system[17] also illustrates this balance between physical and chemical effects. Above 360 K, H^E is positive throughout the entire composition range. At these higher temperatures the specific effects that produce a negative heat of mixing at 298 K are absent, and endothermal physical interactions now predominate to give an equimolar H^E of 600 J mol^{-1}. As a general conclusion, therefore, water–alcohol mixtures involve endothermic dispersive-type interactions such as occur in any normal mixture of dissimilar molecules, although the effect of H-bonding may predominate at lower temperatures and shorter alkyl chain lengths.

As noted earlier, the origin of the cosolvent effect shown by 1-propanol–water for PMMA is unlikely to have any free volume origin. Using the procedures already described[5,6] and values of T_1^* from *Figure 3*, the temperature separation of the contour for PMMA (830×10^3) on the temperature scale, can be fitted as a function of solvent composition by equation (1) to yield values of c_1v^2. These are plotted also in *Figure 3* and pass through a minimum in the same fashion as observed for

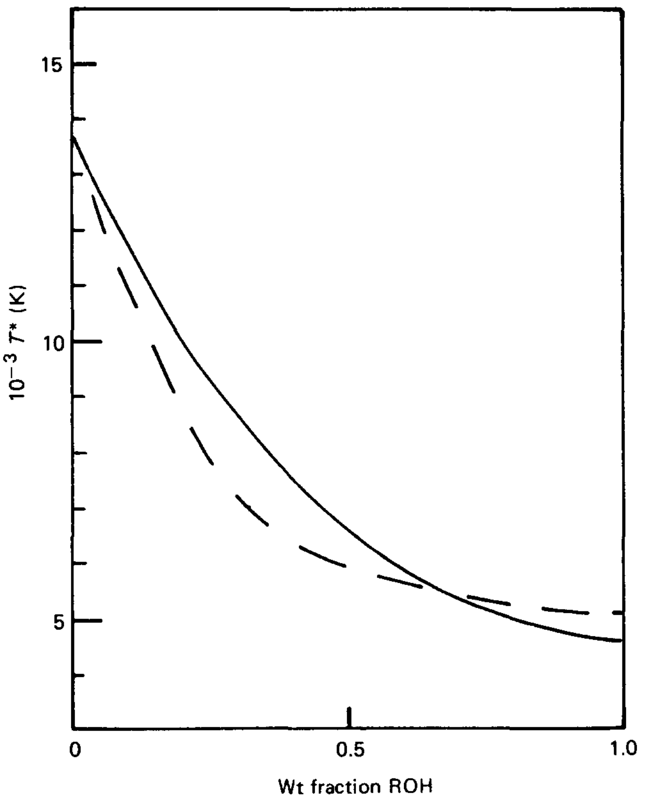

Figure 4 Temperature reduction parameter (T_1^*) for water–methanol (———) and for water-2-propanol (– – –) calculated from literature expansion data[10,11]

other cosolvent systems[5,6]. Thus, cosolvency is manifested as an enhanced enthalpic interaction at an optimum composition of 0.8 volume fraction alcohol.

Minimization of the overall enthalpic interaction can be rationalized at the molecular level by the site model proposed earlier. Each component of the cosolvent mixture has a preferred site(s) of interaction on the polymer (at which its individual exchange or contact energy is a minimum) and when the two act in concert, so to speak, the overall solvation of the coil is enhanced. In the absence of H-bond formation the endothermic component of H^E for water+alcohol is indicative of molecular dissimilarity and thus these two components should minimize their respective contact interactions at different sites on PMMA. Cosolvency in this system can be argued to have the same origin as in systems without specific effects. The fact that the optimum cosolvency in 2-propanol–water occurs in the solvent composition range with a positive H^E, is in accord with this concept. Also not at variance is the behaviour of the other alcohol mixtures. Both 1-propanol and t-butanol combine with water endothermically in the range of observed PMMA solubilization, and the aqueous mixtures with ethanol and methanol are solvents at successively higher temperatures where H-bonding is essentially absent and H^E is again positive.

Implicit in this discussion, and the site model itself, is the requirement for each of the components of a cosolvent to have at least some affinity for the polymer. In the case of the alcohols this is demonstrated since all are solvents at appropriate temperatures (and pressures). For water, however, there is no strong evidence of any such affinity. Diffusion studies[18] of water in alkyl methacrylate polymers show the heat of sorption becoming more exothermic as the alkyl group becomes smaller and less shielded, indicating some possible interaction of the diffusant with the carbonyl group. Diffusion of water into the isotactic polymer does, in fact, result in a minor amount of swelling. This may be interpreted[19] as an interaction at a polar site. However, the heat of dilution obtained from diffusion studies is almost zero, a finding which is consistent with simple sorption into microcavities, to form H-bonded clusters, with little physical interaction with the host polymer[18]. Thus, in contrast to the systems previously studied, it appears that cosolvency in the present case can occur even though the contact of one component must result in the expenditure of an extremely high exchange energy.

The possibility of other favourable contributions from the mixture remains open to discussion. The mixing of water with a species (the alcohol) which is part hydrophilic, part hydrophobic will itself bring about changes. The most obvious is the hydration of the hydroxyl function of the alcohol by H-bonding. Such a modified alcohol is unlikely to have substantially different solvating properties (consisting as it does still of a polar and a non-polar segment), but one could envisage this as a 'localization' mechanism for water molecules which reduces their potential for more energetically expensive contacts with the solute.

A second modification, for which there is thermodynamic evidence, is the structural modification of water in the presence of dissolved hydrocarbons. Heat capacity measurements[20] show a significant increase over that expected for solution and this is interpreted[21] as resulting from the reorganization of loosely bound water molecules into the more ordered 'ice-like' structure. The immediate layer of water molecules in contact with the hydrocarbon surface is thus more tightly H-bonded than in 'normal' bulk water. This breaking up of the usual water structure has also been used to explain the results of ionic conductivity measurements in certain aqueous mixtures[22]. The resulting properties of such modified water structures probably depend more upon physical interactions, rather than H-bonds, which are now involved with the maintenance of the modification.

A precise explanation of the cosolvent action of water–alcohol mixtures for PMMA is elusive. The site model is not completely convincing in this instance, as is the effect of some modified alcohol species. The situation may also be explained in some part by the state of water in mixtures with hydrocarbon surfaces. However, a rather more simplistic picture may suffice at the present state of knowledge. PMMA does possess a contact (the carbonyl group) with which a water molecule can interact favourably in a 'like contacting like' manner and, additionally, by potential H-bond formation. Perhaps the alcohol acts simply as a 'carrier' or diluent which allows this favourable contact to be more readily made. This ability of water to interact with an adequately deshielded carbonyl is hinted at by the diffusion results already mentioned[18] and is also implied in the description given by Cooper *et al.*[23] of the accelerated dissolution of PMMA in water–alcohol mixtures. In this latter case, albeit of a kinetic phenomenon, plasticization by the small, rapidly diffusing, water molecule is envisaged.

REFERENCES

1 Cowie, J. M. G., Garay, M. T. and McEwen, I. J. *Polymer* 1986, **27** (*Commun.*), 122

2 Whipps, P. Phillips Research Laboratories, Redhill, Surrey, England, personal communication

3 Cowie, J. M. G. and McEwen, I. J. *J. Chem. Soc., Faraday Trans. I* 1974, **70**, 171

4 Cowie, J. M. G. and McEwen, I. J. *Macromolecules* 1974, **7**, 291

5 Cowie, J. M. G. and McEwen, I. J. *Macromolecules* 1984, **17**, 755

6 Cowie, J. M. G. and McEwen, I. J. *J. Chem. Soc., Faraday Trans. I* 1984, **80**, 905

7 Cowie, J. M. G. and McEwen, I. J. *J. Chem. Soc., Faraday Trans. I* 1976, **72**, 526

8 Tuzar, Z. and Kratochvil, P. *Collect. Czech. Chem. Commun.* 1967, **32**, 3358

9 Lath, D. and Vasko, M. Polymer Institute, Slovak Academy of Sciences, Bratislava, Czechoslovakia, personal communication

10 Kimel, W. R. and Mikhail, S. Z. *J. Chem. Eng. Data* 1961, **6**, 533

11 Lebo, R. H. *J. Am. Chem. Soc.* 1921, **43**, 1005

12 Franks, F. and Ives, D. J. G. *Q. Rev. Chem. Soc.* 1966, **20**, 1

13 Lama, R. F. and Benjamin, C.-Y. Lu. *J. Chem. Eng. Data* 1965, **10**, 216

14 Goodwin, S. R. and Newsham, D. M. T. *J. Chem. Thermodynamics* 1972, **4**, 31

15 McGlashan, M. L. *Annu. Rep. Chem. Soc.* 1962, **59**, 73

16 Cowie, J. M. G. and McEwen, I. J. *Polymer* 1983, **24**, 1453

17 Larkin, J. A. *J. Chem. Thermodynamics* 1975, **7**, 137

18 Barrie, J. A. and Machin, D. J. *Trans. Faraday Soc.* 1971, **67**, 244

19 Miyaga, M. T. and Tanaka, K. *Polymer* 1975, **16**, 441

20 Arnett, E. M., Kover, W. B. and Carter, J. V. *J. Am. Chem. Soc.* 1969, **91**, 4028

21 Nemethy, G. and Sheraga, H. A. *J. Chem. Phys.* 1962, **36**, 3401

22 Horne, R. A., Johnson, D. S. and Young, R. P. *J. Phys. Chem.* 1968, **72**, 866

23 Cooper, W. J., Krasicky, P. D. and Rodriguez, F. *J. Appl. Polym. Sci.* 1986, **31**, 65