Phase behaviour of blends of poly(acetonyl methacrylate) with poly(styrene-*co*-acrylonitrile) and poly(*p*-methylstyrene-*co*-acrylonitrile)

Y. F. Chong and S. H. Goh*
Department of Chemistry, National University of Singapore, Singapore 0511
(Received 23 April 1991; accepted 20 May 1991)

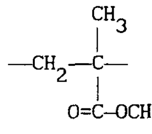
The miscibility of poly(acetonyl methacrylate) (PACMA) with poly(styrene-*co*-acrylonitrile) (SAN) and poly(*p*-methylstyrene-*co*-acrylonitrile) (*p*MSAN) has been studied by differential scanning calorimetry. PACMA is miscible with SAN having acrylonitrile (AN) contents between 33 wt% and 58 wt% and with *p*MSAN having AN contents between 43 wt% and 61 wt%. Three segmental interaction parameters, $\chi_{ACMA/S}$, $\chi_{ACMA/pMS}$ and $\chi_{ACMA/AN}$, were found to be 0.15, 0.22 and 0.24, respectively. The results obtained for PACMA are compared to those of poly(n-propyl methacrylate) and poly(isopropyl methacrylate). The miscibility behaviour is discussed in terms of the binary interaction model as well as the non-hydrogen-bonded solubility parameter concept.

(Keywords: blends; phase behaviour; poly(acetonyl methacrylate); lower critical solution temperature; solubility parameter)

INTRODUCTION

A wide range of polymethacrylates, including poly(methyl methacrylate) (PMMA)[1–3], poly(ethyl methacrylate) (PEMA)[1], poly(n-propyl methacrylate) (PnPMA)[1], poly(chloromethyl methacrylate) (PCMMA)[4], poly(2-chloroethyl methacrylate) (PCEMA)[5], poly(tetrahydropyranyl-2-methacrylate) (PTHPMA)[6] and poly(cyclohexyl methacrylate) (PCHMA)[7], are miscible with poly(styrene-*co*-acrylonitrile) (SAN) over a certain copolymer composition range. Blends of these polymethacrylates with poly(*p*-methylstyrene-*co*-acrylonitrile) (*p*MSAN) also exhibit miscibility windows[5–9]. However, polymethacrylates with bulky alkyl pendent groups such as poly(isopropyl methacrylate) (PiPMA) and poly(n-butyl methacrylate) (PnBMA) are immiscible with SAN over the entire copolymer composition range[1].

We have earlier reported on the miscibility of poly(acetonyl methacrylate) (PACMA)[10–12]. PACMA is miscible with poly(vinylidene fluoride) (PVDF), poly(vinyl chloride) (PVC) and poly(α-methylstyrene-*co*-acrylonitrile) (αMSAN) containing 30 wt% acrylonitrile (AN). We have found that while PVDF is immiscible with PnPMA and PiPMA, it is miscible with PACMA, indicating the importance of the additional carbonyl group in PACMA in achieving miscibility. We now report the miscibility of PACMA with SAN and *p*MSAN, and the miscibility behaviour of the blends is compared to those blends containing PnPMA and PiPMA.



$$-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle O{=}C{-}OCH_2COCH_3}{C}}-$$

PACMA [also known as poly(2-oxopropyl methacrylate)]

EXPERIMENTAL

PACMA was prepared by the method described elsewhere[10,11]. SAN with AN contents of 30 and 25 wt% were obtained from Scientific Polymer Products, Inc. while SAN with 22 wt% AN was provided by Monsanto. Other SAN and *p*MSAN samples were prepared by solution polymerization in 2-butanone (MEK) [a mixture of MEK and dimethylformamide (DMF) was used for preparation of copolymers with high AN contents] at reflux temperature for 4 h using 0.30 wt% AIBN as initiator. The AN contents of the copolymers were determined by elemental analysis for nitrogen. In the following discussion, the number after SAN or *p*MSAN denotes the weight percentage of AN in the copolymer. The characteristics of the copolymers are listed in *Table 1*.

All the blends of PACMA were cast from DMF at 100°C. They were then dried *in vacuo* at 90°C for at least 3 days. The glass transition temperature (T_g) of various samples was measured with a Perkin–Elmer DSC-4 differential scanning calorimeter, using a heating rate of 20°C min^{-1}. All the miscible blends were examined for the existence of the lower critical solution temperature (*LCST*) behaviour by the method described elsewhere[10,11].

---

* To whom correspondence should be addressed

0032-3861/92/061289-04

Table 1 T_g and molecular weight information of SAN and *p*MSAN

Sample	$\bar{M}_w$[a]	$\bar{M}_n$	T_g (°C)
SAN22.0(35.6)[b]	116000	51000	103
SAN25.0(39.5)	156000	66000	102
SAN30.0(45.7)	125000	61000	100
SAN33.4(49.6)	114000	52000	110
SAN34.5(50.8)	29000	21000	110
SAN40.0(56.7)	47000	31000	110
SAN43.6(60.3)	43000	27000	110
SAN46.6(63.1)	$[\eta] = 0.48$ dl g^{-1}		106
SAN50.9(67.0)	$[\eta] = 0.65$ dl g^{-1}		105
SAN58.0(73.0)	$[\eta] = 0.68$ dl g^{-1}		110
*p*MSAN29.1(47.7)	56000	34000	105
*p*MSAN32.3(51.5)	62000	38000	104
*p*MSAN39.6(59.3)	59000	33000	115
*p*MSAN43.5(63.2)	57000	39000	115
*p*MSAN45.3(64.8)	$[\eta] = 0.53$ dl g^{-1}		113
*p*MSAN51.2(70.0)	$[\eta] = 0.39$ dl g^{-1}		113
*p*MSAN53.2(71.7)	$[\eta] = 0.44$ dl g^{-1}		110
*p*MSAN61.1(77.8)	$[\eta] = 0.36$ dl g^{-1}		115

[a] Molecular weights were obtained by g.p.c. measurements using polystyrene standards. The intrinsic viscosity, $[\eta]$, was measured in DMF at 22°C

[b] Values in parentheses are the molar percentage of AN in the copolymer

RESULTS AND DISCUSSION

PACMA/SAN blends

Blends of PACMA with SAN containing 33.4, 34.5, 40.0, 43.6, 46.6 and 50.9 wt% AN were transparent and each exhibited a single, composition-dependent glass transition. All these transparent blends underwent phase separation upon heating and the cloud point curves are shown in *Figure 1*. All the blends containing SAN22, SAN25 and SAN30 were cloudy and each showed two T_gs. However, the upper T_g values of all these blends were lower than those of the SAN samples, indicating the presence of PACMA in the SAN-rich phase.

PACMA/SAN58 blends containing 50, 75 and 90 wt% SAN58 were clear and only one T_g was observed in each blend. *LCST* behaviour was observed in each of these three blends. The cloud point curve for the PACMA/SAN58 blend system is shown in *Figure 2*. However, blends containing 10 and 25 wt% SAN58 were cloudy and each showed two distinct glass transitions, indicating their phase-separated nature. Hence, the miscibility of PACMA/SAN58 blends depends on their compositions. The present results indicate that blends containing SAN58 are near the verge of immiscibility in the phase diagram as shown in *Figure 3*. PACMA is concluded to be miscible with SAN having AN contents between 33 wt% and 58 wt%.

PACMA/pSAN blends

The T_g–composition curves for various PACMA/*p*MSAN blends are shown in *Figure 4*. Blends of PACMA with *p*MSAN containing 43.5, 45.3, 51.2 and 53.2 wt% AN were transparent, and each showed only one composition-dependent T_g, indicating complete miscibility within this range of AN contents. All these miscible blends exhibited *LCST* behaviour upon heating. Blends of PACMA with *p*MSAN containing 29.1, 32.3 and 39.6 wt% AN were cloudy and each showed two T_gs.

Except for the blends containing 10 and 25 wt% *p*MSAN61.1, the other PACMA/*p*MSAN61.1 blends were transparent and each showed one glass transition. *LCST* behaviour was observed for all these miscible

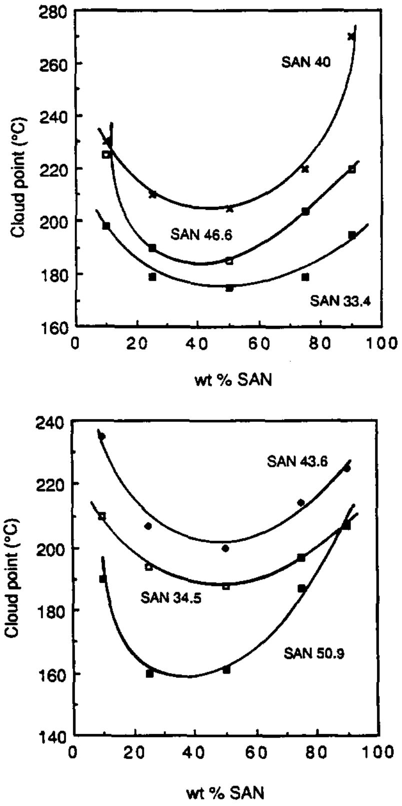


Figure 1 Cloud point curves of various miscible PACMA/SAN blends

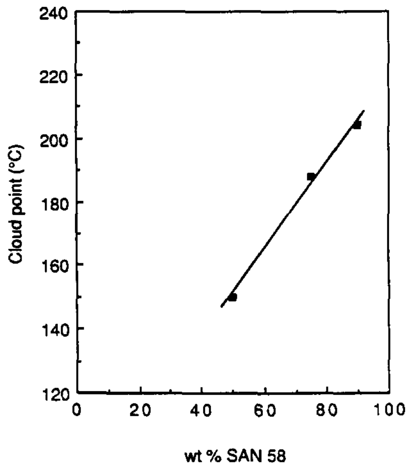


Figure 2 Cloud point curve for PACMA/SAN58 blends

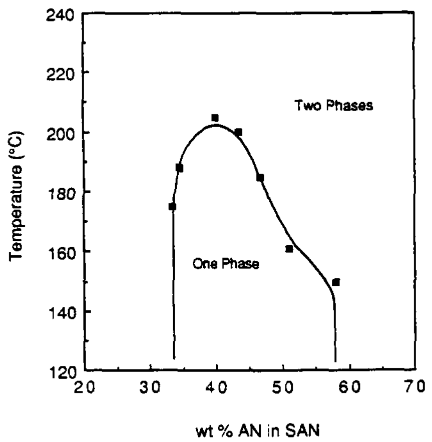


Figure 3 Phase diagram of PACMA/SAN (50/50) blends

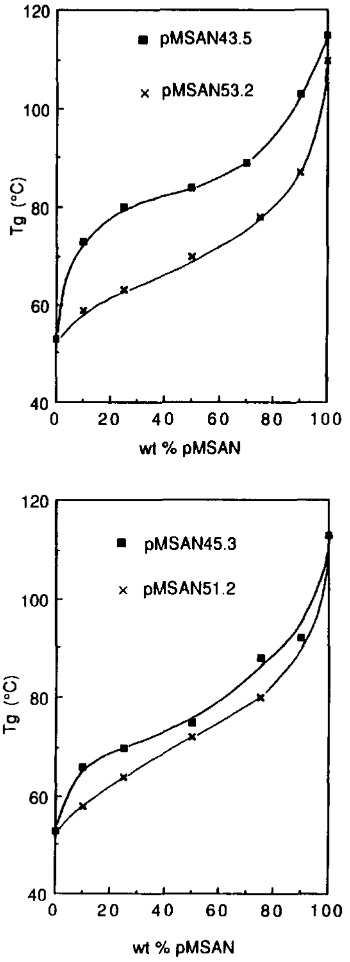


Figure 4 T_g–composition curves for miscible PACMA/*p*MSAN blends

blends. PACMA/*p*MSAN61.1 containing 10 and 25 wt% *p*MSAN61.1 were cloudy and each showed two T_gs. The T_g–composition and cloud point curves for PACMA/*p*MSAN61.1 blends are shown in *Figures 5a* and *b*. The results indicate that the miscibility of PACMA/*p*MSAN61.1 blends is composition-dependent. Hence, PACMA is miscible with *p*MSAN containing 43–61 wt% AN. The phase diagram is shown in *Figure 6*.

Segmental interaction parameters

Table 2 summarizes the miscibility behaviour of PACMA, PnPMA and PiPMA with SAN and *p*MSAN. Both PnCPMA and PACMA are miscible with SAN and *p*MSAN, but the miscibility windows for the PACMA blends shift towards the high AN ends.

The miscibility behaviour of a homopolymer A/copolymer BC blend system is often explained by a simple binary interaction model[13–15]. The net interaction parameter χ_{blend} is related to various segmental interaction parameters by

$$\chi_{\text{blend}} = y\chi_{A/C} + (1-y)\chi_{A/B} - y(1-y)\chi_{B/C} \quad (1)$$

where y is the volume fraction of C in the copolymer. The criterion for miscibility is that $\chi_{\text{blend}} < \chi_{\text{crit}}$ where

$$\chi_{\text{crit}} = 1/2(N_1^{-1/2} + N_2^{-1/2})^2$$

where N_1 and N_2 are the degrees of polymerization of A and BC. χ_{crit} depends more on the smaller N value and it approaches zero when both N_1 and N_2 are sufficiently large. The miscibility behaviour of a homo-

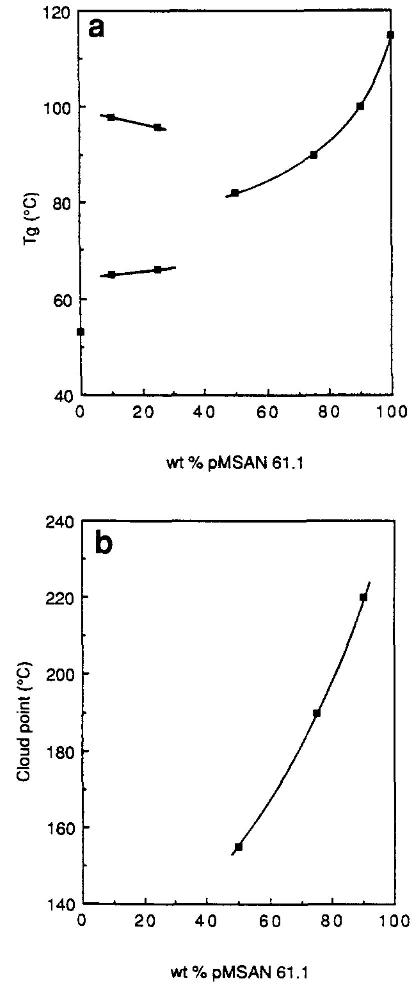


Figure 5 (a) T_g–composition curve for PACMA/*p*MSAN61.1 blends. (b) Cloud point curve for PACMA/*p*MSAN61.1 blends

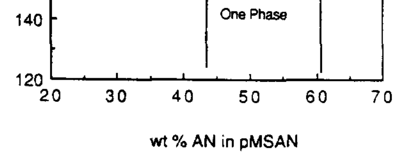


Figure 6 Phase diagram of PACMA/*p*MSAN (50/50) blends

Table 2 Phase behaviour of PACMA, PnPMA and PiPMA with SAN and *p*MSAN

Blend system	Miscibility range (wt% AN)
PACMA/SAN	33–58
PACMA/*p*MSAN	43–61
PnPMA/SAN	2–25[1]
PnPMA/*p*MSAN	6–28[9]
PiPMA/SAN	Immiscible[1]
PiPMA/*p*MSAN	Immiscible[9]

polymer/copolymer blend system enables the evaluation of various segmental interaction parameters. On the other hand, a knowledge of these interaction parameters enables the prediction of the phase behaviour of a blend system[16,17].

For the present two blend systems, $\chi_{S/AN}$ and $\chi_{pMS/AN}$ are 0.829 and 0.91 respectively[3,8], and χ_{crit} is taken as zero. Hence, the other three interaction parameters can be evaluated from equation (1).

For the PACMA/SAN blend system, the miscibility boundaries are at 33 and 58 wt% AN, corresponding to y values of 0.32 and 0.56. Application of equation (1) leads to values of 0.15 and 0.25 for $\chi_{ACMA/S}$ and $\chi_{ACMA/AN}$, respectively. For the PACMA/*p*MSAN blends, the boundaries are at 43 and 61 wt% AN, corresponding to y values of 0.41 and 0.59, respectively. Similarly, application of equation (1) leads to a value of 0.22 for both $\chi_{ACMA/pMS}$ and $\chi_{ACMA/AN}$. The $\chi_{ACMA/AN}$ values obtained from the PACMA/SAN and PACMA/*p*MSAN blend systems are in good agreement with each other. Therefore, the three segmental interaction parameters, $\chi_{ACMA/S}$, $\chi_{ACMA/pMS}$ and $\chi_{ACMA/AN}$ are taken to be 0.15, 0.22 and 0.24, respectively.

It is also noted that $\chi_{ACMA/pMS}$ is larger than $\chi_{ACMA/S}$. This is consistent with other reports that the segmental interaction parameter between *p*-methylstyrene (*p*MS) and the other segment is larger than that between styrene (S) and the same reference segment[6–8,18–20].

$\chi_{nPMA/pMS}$ and $\chi_{nPMA/AN}$ are 0.018 and 0.64, respectively[9], and $\chi_{nPMA/S}$ is estimated to be 0.013 using the results of Fowler *et al.*[1]. Thus $\chi_{ACMA/S}$ and $\chi_{ACMA/pMS}$ are substantially larger than $\chi_{nPMA/S}$ and $\chi_{nPMA/pMS}$, but $\chi_{ACMA/AN}$ is smaller than $\chi_{nPMA/AN}$. These χ values imply that the presence of an additional carbonyl group in the pendent group of the polymethacrylate reduces its repulsive interaction with the AN segment but enhances the repulsive interaction with both S and *p*MS segments. Based on the binary interaction model, the immiscibility of PiPMA with SAN and *p*MSAN can be attributed to larger $\chi_{iPMA/S}$, $\chi_{iPMA/pMS}$ and $\chi_{iPMA/AN}$ values as compared to the corresponding χ involving the nPMA segment such that χ_{blend} is larger than χ_{crit} at all y values.

Recently, Coleman *et al.*[21] proposed a simple guide to predict polymer miscibility based on the non-hydrogen-bonded solubility parameter (δ) concept. For polymers which interact with weak dispersive forces only, the δ values of the two polymers must be closely matched [$<0.2\,(\mathrm{J\,cm^{-3}})^{1/2}$] in order for the polymers to be miscible with each other. For polymers able to interact via stronger interactions such as hydrogen bonding, a mismatch between the δ values as large as 5.1–6.1 $(\mathrm{J\,cm^{-3}})^{1/2}$ can be tolerated. They also used this concept to explain the miscibility of homopolymer/copolymer blends such as PVC/poly(butadiene-*co*-acrylonitrile) blends.

Using the group molar attraction constants given by Coleman *et al.*[21], the δ values for PnPMA, PiPMA and PACMA are found to be 18.0, 17.4 and 21.3 $(\mathrm{J\,cm^{-3}})^{1/2}$, respectively. The δ values for SAN and *p*MSAN are in the range 19.4–27.4 and 19.2–27.4 $(\mathrm{J\,cm^{-3}})^{1/2}$, respectively, depending on the copolymer composition. The differences in δ values for PnPMA with SAN and *p*MSAN are smaller than those for PiPMA. The immiscibility of PiPMA with SAN and *p*MSAN can be attributed to a larger mismatch in δ values. PACMA has a larger δ value than the PnPMA and PiPMA, owing to the presence of the additional carbonyl group in its pendent group. PACMA is expected to be miscible with SAN and *p*MSAN having higher AN contents, and the expectation is consistent with our experimental results.

The difference in δ between PnPMA and PS is $1.4\,(\mathrm{J\,cm^{-3}})^{1/2}$ and that between PnPMA and PAN is $9.4\,(\mathrm{J\,cm^{-3}})^{1/2}$. It is then expected that $\chi_{nPMS/S}$ is significantly smaller than $\chi_{nPMS/AN}$. Based on the same consideration, $\chi_{ACMA/S}$ is expected to be larger than $\chi_{nPMA/S}$ and $\chi_{ACMA/AN}$ to be smaller than $\chi_{nPMA/AN}$. All the expectations are consistent with the segmental interaction parameters evaluated from the phase behaviour. The non-hydrogen bonded solubility parameter approach appears to be able to explain, at least qualitatively, the difference in the miscibility behaviour of PnPMA, PiPMA and PACMA.

In conclusion, the presence of the additional carbonyl group in the PACMA segment has a significant effect on its miscibility behaviour as compared with PnPMA and PiPMA.

ACKNOWLEDGEMENT

Financial support of this study by the National University of Singapore is gratefully acknowledged.

REFERENCES

1 Fowler, M. E., Barlow, J. W. and Paul, D. R. *Polymer* 1987, **28**, 1177

2 Suess, M., Kressler, J. and Kammer, H. W. *Polymer* 1987, **28**, 957

3 Cowie, J. M. G. and Lath, D. *Makromol. Chem., Macromol. Symp.* 1988, **16**, 103

4 Goh, S. H. and Lee, S. Y. *J. Appl. Polym. Sci.* 1990, **41**, 1391

5 Neo, M. K., Lee, S. Y. and Goh, S. H. *Eur. Polym. J.* 1991, **27**, 831

6 Chong, Y. F. and Goh, S. H. *Polymer* in press

7 Chong, Y. F. and Goh, S. H. *Polymer* in press

8 Goh, S. H. and Lee, S. Y. *Eur. Polym. J.* 1990, **26**, 715

9 Goh, S. H., Siow, K. S. and Lee, S. Y. *Eur. Polym. J.* 1991, **27**, 921

10 Chong, Y. F., Lee, S. Y. and Goh, S. H. *Eur. Polym. J.* 1990, **26**, 1145

11 Chong, Y. F., Lee, S. Y. and Goh, S. H. *Eur. Polym. J.* 1990, **26**, 1207

12 Goh, S. H., Lee, S. Y., Chong, Y. F., Neo, M. K. and Leong, C. L. *Macromolecules* 1991, **24**, 806

13 Kambour, R. P., Bendler, J. T. and Bopp, R. C. *Macromolecules* 1983, **16**, 753

14 ten Brinke, G., Karasz, F. E. and MacKnight, W. J. *Macromolecules* 1983, **16**, 1827

15 Paul, D. R. and Barlow, J. W. *Polymer* 1984, **25**, 487

16 Cowie, J. M. G., McEwen, I. J. and Reid, V. C. M. *Polymer* 1990, **31**, 486

17 Cowie, J. M. G., Reid, V. C. M. and McEwen, I. J. *Polymer* 1990, **31**, 905

18 Su, A. C. and Fried, J. R. *Am. Chem. Soc. Symp. Ser.* 1989, **391**, 155

19 Goh, S. H. and Lee, S. Y. *Eur. Polym. J.* 1989, **25**, 571

20 Maconnachie, A., Fried, J. R. and Tomlins, P. E. *Macromolecules* 1989, **22**, 4606

21 Coleman, M. M., Serman, C. J., Bhagwagar, D. E. and Painter, P. C. *Polymer* 1990, **31**, 1187