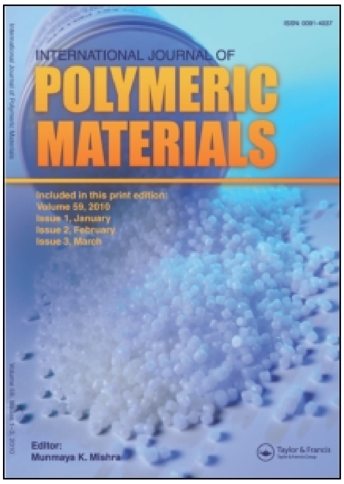

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Blends of Poly(N-vinyl-2-pyrrolidone)/Poly(dialkyl itaconates) and Poly(methacrylates)

Alejandra Opazo[a]; Ligia Gargallo[a]; Deodato Radić[a]
[a] Dpto. de Química Fisica, Facultad de Química, Pontificia Universidat Católica de Chile, Santiago 22, Chile

To cite this Article Opazo, Alejandra , Gargallo, Ligia and Radić, Deodato(1994) 'Blends of Poly(N-vinyl-2-pyrrolidone)/Poly(dialkyl itaconates) and Poly(methacrylates)', International Journal of Polymeric Materials, 27: 1, 117 — 125

To link to this Article: DOI: 10.1080/00914039408038299

URL: http://dx.doi.org/10.1080/00914039408038299

Intern. J. Polymeric Mater., 1994, Vol. 27, pp. 117-125
Reprints available directly from the publisher
Photocopying permitted by license only

Amsterdam B.V.
Published under license by
Gordon and Breach Science Publishers SA
Printed in Malaysia

Blends of Poly(N-vinyl-2-pyrrolidone)/ Poly(dialkyl itaconates) and Poly(methacrylates)

ALEJANDRA OPAZO, LIGIA GARGALLO and DEODATO RADIĆ*

Dpto. de Química Fisica, Facultad de Química, Pontificia Universidat Católica de Chile,
Casilla 306, Santiago 22, Chile

(Received June 15, 1994; in final form June 30, 1994)

Blends containing poly(N-vinyl-2-pyrrolidone) (PVP) and poly(dialkyl itaconates) (PDI) and poly(methacrylates) (PMA) with different side chain structures were prepared. Polymer blends of various compositions were studied by Differential Scanning Calorimetry (DSC) and Thermomechanical Analysis (TMA). The effect of the substitution on the lateral chain is also analyzed. One *Tg* value, over the whole range of compositions is observed for the majority of the blends reflecting compatibility. Inmiscible polymer blends are also observed which is apparently dependent on the structure of the side chain.

KEY WORDS Blends, poly(N-vinyl-2-pyrrolidone), poly(dialkyl itaconates), poly(methacrylates), differential scanning calorimetry, thermomechanical analysis.

INTRODUCTION

Polymer blends containing poly(N-vinyl-2-pyrrolidone) (PVP) and poly(monoitaconates) (PMI) have been reported previously.[1] Miscibility and interpolymer complex formation is observed in the majority of such systems, which has been attributed to hydrogen bonding interactions. In fact, poly(monoitaconates) are capable to interact by hydrogen bonding formation through the free carboxyl group. On the other hand in these systems the effect of the side chain structure on the miscibility plays an important role as it was previously reported.[1,2,3] Therefore, in these blends, there are at least two contributions to miscibility. It seems interesting to analyze the effect of the nature and structure of the side chain on the miscibility in related systems, where the carboxyl group of monoitaconates is protected. By this way it is possible to know the influence of the polymer substituents on the miscibility.

However, to our knowledge, no works dealing with blends containing PVP and poly(dialkylitaconates) (PDAI) have been reported. These blends should be of

---

*Author to whom correspondence should be addressed.

interest in order to compare the miscibility behaviour with those reported for blends containing the monosubstituted polymers. If miscibility between these polymers, takes place, this should be the result of different kinds of interactions, such as dipole-dipole interactions, rather than hydrogen bonding. Poly(methacrylates) with different side chains structures could be another system to be considered in order to study interactions in blends where hydrogen bonding are not possible.

The aim of the present work is the study of the compatibility in blends of PVP with poly(methacrylates) and poly(dialkylitaconates) with different side chain structures, in order to investigate the effect of the polymer structure on the miscibility. It is possible, by one hand, to split the effect of the hydrogen bonding interaction from the effect of the polymer structure, by esterification of the carboxyl group of poly(monoitaconates). However, in the case of PDAI there is another factor to be taken into account what is the important increment of the bulkiness of the side chain which could be unfavourable for miscibility. On the other hand, the functionalization of the polymer side group should be another way in order to analyze miscibility in polymer blends. In fact, functionalization of the polymer side group could be a powerful tool to promote polymer-polymer miscibility through specific interactions between polymer side groups. Blends of PVP of different weight average molecular weight, with poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly(dialkyl itaconates) (PDAI), chlorinated poly(methacrylates) (CPMA) and chlorinated poly(dialkylitaconates) (CPDAI) were studied by differential scanning calorimetry (DSC) and thermomechanical analysis (TMA).

EXPERIMENTAL

Monomers and Polymers Preparation

Commercial samples of poly(N-vinyl-2-pyrrolidone) (PVP) of three weigh-average molecular weight Mw: 10000; 24000 and 40000 from Aldrich and labelled as PVP_{10}; PVP_{24} and PVP_{40} were used.

Poly(methacrylates). Poly(methylmethacrylate) (PMMA), poly(ethylmethacrylate) (PEMA), poly(2-chloroethyl methacrylate) (P2CEM), poly(3-chloropropyl methacrylate) (P3CPM) were obtained by radical polymerization. Monomers were synthesized by reaction of methacryloyl chloride with the corresponding alcohols as previously described.[5,6,7]

Poly(dialkylitaconates). Poly(dimethyl itaconate) (PDMI), poly(diethyl itaconate) (PDEI), poly(di-*n*-propyl itaconate) (PDPI), poly(di-2-chloroethyl itaconate) (PD2CEI), poly(di-3-chloropropyl itaconate) (PD3CPI) were obtained by radical polymerization. Monomers were synthesized by reaction of itaconic acid with the corresponding alcohols in toluene using *p*-toluensulphonic acid.[7,8,9]

Preparation of the Blends

Blends of different compositions were prepared by solutions casting using chloroform and then evaporated at room temperature and vacuum dried at 298°K by 72 h. The polymer concentration in the solution was about 2% (w/w).

DSC Measurements

The glass transition temperatures (*Tg*) of the different polymers and blends were measured with a Mettler TA-3000 system equipped with a TC-A 10 Processor with DSC-20 cell and DSC-30 cell for polymers with *Tg* under room temperature.

Polymer samples were dried under reduced pressure in a vacuum oven prior measurements. Samples were weighted into the DSC aluminum pans. Dry nitrogen were used as purge gas and thermograms were measured in the range 308°K to 453°K, for polymers with *Tg* under 308°K, to 280°K, at a scan rate of 10 K/min. Regular calibration of the instrument was carried using pure metal standars.

TMA Measurements

Thermomechanical analysis was carried out using a thermomechanical measuring cell Mettler TMA-40 coupled with a TC-10 A Mettler TA processor. Round films of 50 mm of diameter and thickness between 1.8–2.0 mm were used. Measurements were performed between 308°K and 453°K at a scan rate of 10 K/min. Calibration temperature was performed by means of three metals, In, Sn and Pb. The *Tg* corresponds to the intersection of two regression lines on the plot.

RESULTS AND DISCUSSION

The DSC and TMA thermograms for blends of PVP_{24} with PMMA, PEMA, P2CEM and P3CPM exhibit distinct single glass transition temperatures (*Tg*) what should be indicative of one phase material and therefore these blends could be considered as miscible. Figure 1 shows the variation of *Tg* with composition measured by DSC. Similar behaviour is observed for blends containing PVP_{10}. The effect of the molecular weight of PVP on the miscibility was previously reported.[1,3] PVP_{10} and PVP_{24} are in general miscible with poly(monoitaconates)[1] and poly(2,6-dimethyl-1,4-phenylene oxide)[3] but in blends containing PVP of higher molecular weights phase separation takes place. Nevertheless, miscibility is found in the case of poly(methacrylates) or poly(itaconates) with chlorinated side chains. These results could be attributed to differences in the strength of the interactions involved, due to the increasing of the dipole-dipole interaction. Blends of PVP_{40} with PMMA and PEMA have been reported as inmiscible by Goh *et al.*[10,11,12] while blends of PVP_{40} with different halogenated poly(methacrylates) are miscible but in this case, blends are prepared by casting from dimethylformamide (DMF) while the results reported in the present work correspond to blends obtained by casting from chloroform which is a better solvent for both polymers. The effect of the casting solvent is another factor to take into account in the miscibility of polymer blends.[1]

Figure 2-a shows the variation of *Tg* with composition for blends of poly(dimethylitaconate) (PDMI) with PVP_{24} and PVP_{40}. Distinct single glass transition temperatures (*Tg*) indicating complete miscibility are observed but both systems show a minimum in *Tg*. According to these results PDMI and PVP are miscible in the whole composition range irrespective of the molecular weight of PVP. If we compare the results dealing with the variation of *Tg* with composition

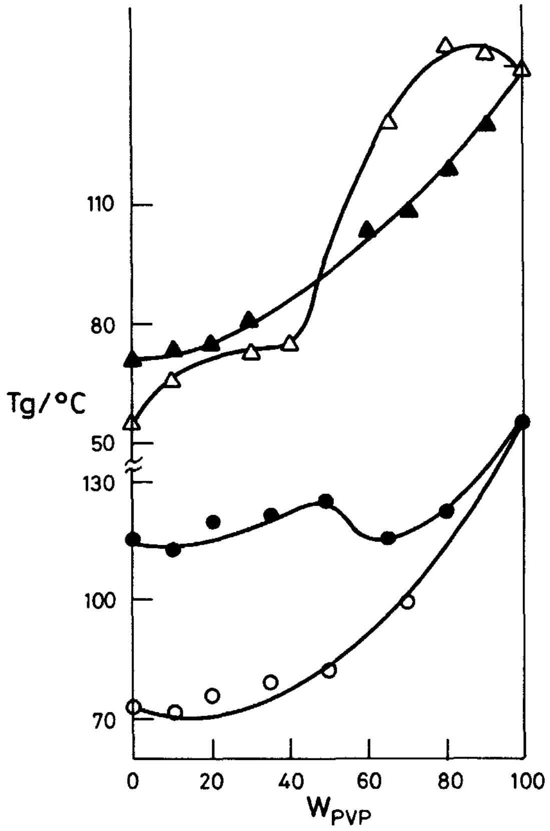

FIGURE 1 Variation of the glass transition temperature (*Tg*) with composition (W_{PVP}) for blends of PVP_{24} with: PMMA (●); PEMA (○); P2CEMA (△) and P3CPMA (▲).

in these systems with those reported for blends of the corresponding poly(monoitaconates) (PMI) with PVP, similarities in the behaviour are observed. In fact, minima in the *Tg* composition diagrams was reported as an evidence of interpolymer complex formation between PVP and PMI, which was attributed to hydrogen bonding interaction, through the free carboxyl group of PMI. In poly(diitaconates) the increasing of the bulkiness of the side chain, because of the existence of two substituents as side chain could be a factor against miscibility, however, for PDMI the existence of one single *Tg* value together with the transparency of the films indicate miscibility. Perhaps the effect of the structure on the miscibility cannot be detected in the first members of the series such as PDMI because it is possible that dipole-dipole interactions be sufficiently strong to maintain miscibility. Increasing the bulkiness of the side chain as in poly(diethyl itaconate) (PDEI) and poly(di-*n*-propyl itaconate) (PDPI) phase separation takes place as can be seen in Figure 2-b. In these Figures it is possible to observe two *Tg* values over the whole composition range corresponding to the *Tg* values of the individual polymers. It is interesting to remark the important change in the miscibility from the dimethyl to the diethyl derivative in the sense that the increasing

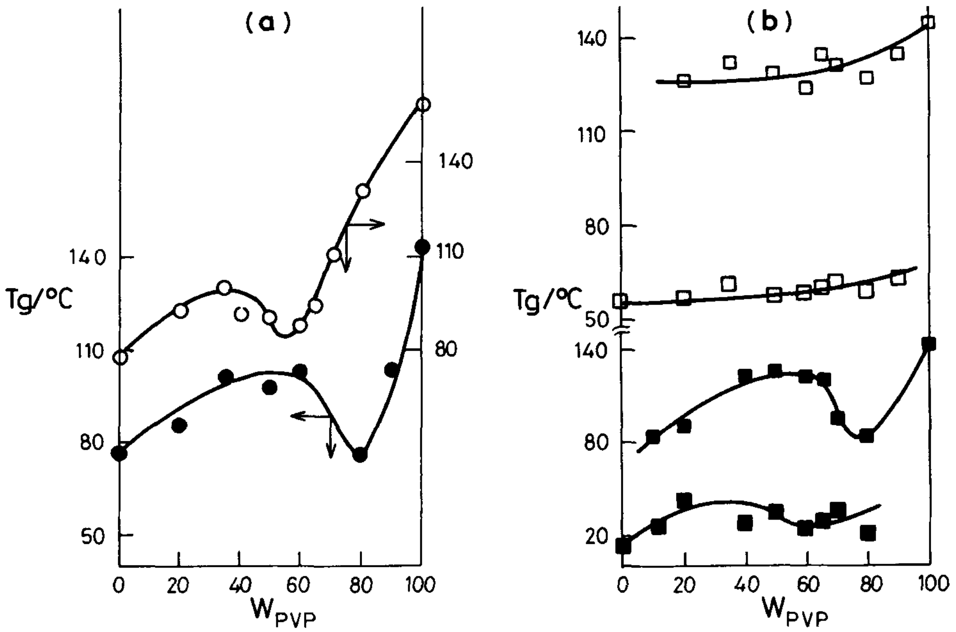

FIGURE 2 Variation of the glass transition temperature (*Tg*) with composition (W_{PVP}) for blends of a) PVP_{24} with PDMI (●) and PVP_{40} with PDMI (○) and b) PVP_{24} with PDEI (□) and PDPI (■).

in one methylene group in the side chain promotes drastically inmiscibility. This could be considered as an effect of the side chain structure on the miscibility, where the strength of the dipole-dipole interaction is not enough to maintain miscibility due to the steric effect of the side chain. In the case of blends containing the corresponding poly(monoitaconates)[1] this effect cannot be detected because the interaction through hydrogen bonding is sufficiently strong to allow the miscibility. Clearly in that case the driving force to miscibility seems to be the interaction through the carboxyl group irrespective on the bulkiness of the side chain.[1,2,3] For blends containing poly(diitaconates) the main factor to be considered should be the size of the side group, taking into account that there are two substituents per repeating unit of the polymer. Therefore, the results shown in Figures 1 and 2 together with those previously reported for blends of PVP and PMI would indicate a clear effect of the substituent on the miscibility. On the other hand the functionalization of the side group with polar substituents should be another way to take into account in the analysis of the effect of the polymer structure on the miscibility. In fact, Goh *et al.*[1,2,3] have recently reported that functionalized poly(methacrylates) with halogenated substituents are miscible with PVP_{40} while in blends with non-functionalized components phase separation is observed. Figure 3 represents the dependence of *Tg* with composition for blends of PVP_{24} and PVP_{10} with halogenated poly(diitaconates) i.e. poly(di-2-chloroethyl itaconate) (PD2CEI) and poly(di-3-chloropropyl itaconate) PD3CPI. In Figure 3 we can observe that samples show distinct single glass transition temperatures intermediate to those corresponding to the parent homopolymers. The monotonous variation of *Tg* as

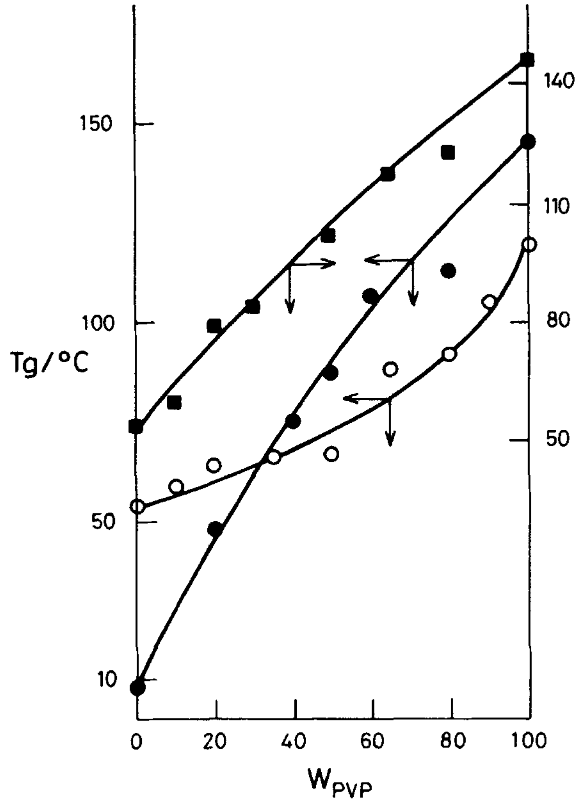

FIGURE 3 Variation of the glass transition temperature (*Tg*) with composition (W_{PVP}) for blends of PVP_{24} with: PD2CEI (■); PD3CPI (●); and PVP_{10} with PD2CEI (○).

function of composition is indicative of one phase material. Therefore, chlorination of poly(dialkylitaconates) promotes miscibility with PVP_{10} and PVP_{24} in the higher members of the series. Tables I and II summarize the *Tg* values obtained by DSC and TMA for the different blends studied at several compositions. In general good agreement is found using both techniques.

It should be possible to analyze *Tg*-composition diagrams in those miscible systems by using the Gordon-Taylor equation[13]:

$$Tg = \frac{w_1 Tg_1 + k w_2 Tg_1}{w_1 + k w_2} \quad (1)$$

where *Tg* is the glass transition temperature of the blend and Tg_i are the glass transition temperatures of the corresponding homopolymers, w_i are the corresponding weight fractions and *k* is a parameter related with the degree of curvature of the *Tg*-composition plot dealing with the strength of the interaction. The *k* parameter of the Gordon-Taylor[13] equation can be taken as a semiquantitative

TABLE I

Tg values obtained by DSC and TMA for blends of PVP_{24} with poly(methacrylates) and poly(diitaconates) at different compositions (%w/w)

PVP_{24}	PMMA		PEMA		PDMI		PDEI		PDPI	
%w/w	DSC	TMA	DSC	TMA	DSC	TMA	DSC	TMA	DSC	TMA
0	116.9	100.1	74.5	78.4	78.3	85.5	56.3	83.1	14.1	-
10	112.7	109.3	72.0	73.7	-	-	-	-	29.5	-
	-	-	-	-	-	-	-	-	85.7	-
20	121.5	11.6	75.0	74.5	86.0	82.0	56.9	-	43.0	-
	-	-	-	-	-		127.8	-	93.0	
35	121.1	116.6	80.0	79.5	102.7	95.0	60.3	-	-	-
							133.0			
40	-	-	-	-	90.5	88.0	-	-	26.6	-
									124.0	-
50	126.2	112.8	82.7	81.1	100.0	90.0	58.3	-	34.6	-
							129.1		127.6	-
60	119.8	117.6	-	-	103.7	100.0	59.0	-	21.2	-
							122.7			
65	115.0	105.0	110.6	96.4	-	-	61.2	-	100.6	-
	-	-	-	-	-		135.0	-	-	-
	-	-	-	-	-	-	-	-	38.0	-
70	-	-	100.0	86.0	-	-	60.8	-	95.7	-
	-	-	-	-	-	-	131.6	-	-	-
80	121.4	107.4	118.7	88.9	80.1	65.2	59.5	-	20.0	-
	-	-	-	-	-	-	127.4	-	85.7	-
90	124.3	141.7	-	-	93.5	80.0	62.1	-	-	-
	-	-	-	-	-	-	135.3	-	-	-
PVP_{10}	105.6	116.6	-	-	-	-	-	-	-	-
PVP_{24}	145.4	128.6	-	-	-	-	-	-	-	-
PVP_{40}	160.0	154.3	-	-	-	-	-	-	-	-

measure of the strength of the interaction between the components of the blends, as Belorgey and Prud'homme[14] have pointed out. In the *Tg*-composition plots concavity is observed even in polymer-polymer blends which presents strong interactions.[15-19] In the present work we have determined the *k* values for blends containing only poly(methacrylates), because in those containing poly(dialkylitaconates) it is very difficult due to the shape of the curves and probably due to the existence of interpolymer complexes. The *k* parameters obtained ranging between 0.022 to 0.186 reflect fairly interaction strength.

TABLE II

Tg values obtained by DSC and TMA for blends containing PVP_{24} and chlorinates poly(methacrylates) and poly(diitaconates) at different compositions (%w/w)

PVP_{24}	PD2CEI		PD3CPI		P2CEMA		P3CPMA	
%w/w	DSC	TMA	DSC	TMA	DSC	TMA	DSC	TMA
0	54.0	59.0	8.8	-	72.7	84.7	55.3	57.5
10	60.0	65.2	-	-	74.2	66.4	67.0	-
20	79.6	75.5	48.2	-	68.6	64.8	-	-
30	-	-	-	-	76.7	67.5	72.5	-
35	84.3	90.0	-	-	-	-	-	-
40	-	-	75.0	-	73.1	61.4	76.4	55.0
50	103.7	95.2	87.1	-	81.7	93.7	77.0	65.1
60	-	-	108.5	-	97.1	115.4	133.1	85.0
65	117.7	125.1	-	-	-	-	-	-
70	-	-	-	-	99.3	120.0	160.8	124.5
80	122.3	104.3	111.7	-	118	100.4	151.7	94.6
90	-	-	-	-	130	113.2	152.1	-
PVP_{24}	145.4	128.6	-	-	-	-	-	-

CONCLUSIONS

Blends of poly(*N*-vinyl-2-pyrrolydone) (Mw: 10000 and 24000) with poly(methacrylates), poly(dialkyl itaconates) and the corresponding chlorinated derivatives show a very interesting behaviour from miscibility point of view. Blends containing poly(methacrylates) exhibit distinct single glass transition temperatures. Therefore, these blends are miscible over the whole composition range. Miscibility is also found in those blends with poly(dimethyl itaconate). Phase separation takes place when the bulkiness of the side chain increases as is the case of pol(diethyl and dipropyl itaconate) but when the side chain is functionalized by chlorine groups, miscibility is promoted what should be indicative that dipole-dipole interactions play an important role on the miscibility irrespective of the steric hindrance due to the bulkiness of the side chain. Therefore, in blends of PVP_{24} with poly(monoitaconates) previously reported[1] it should be necessary to take into account dipole-dipole interaction and therefore miscibility can be attributed to at least two contribution i.e. hydrogen bonding and electrostatic interaction.

Acknowledgments

We express our thanks to Fondo Nacional de Desarrollo Científico y Technológico (FONDECYT). A. Opazo Thanks to FUNDACION ANDES for a Doctoral fellow.

References

1. D. Radić, A. Opazo, X. Guerrero and L. Gargallo, *Intern. J. Polymeric Mater.*, **18**, 19 (1992).
2. D. Radić and L. Gargallo, *Thermochimica Acta*, **180**, 241 (1991).
3. A. Opazo, L. Gargallo and D. Radić, *Polym. Bull.*, **27**, 205 (1991).
4. O. Olabisi, L. M. Robeson and M. T. Shaw, "Polymer-Polymer Miscibility," Academic Press, New York, 1979.
5. J. G. Burtle and W. N. Turek, *J. Org. Chem.*, **19**, 1567 (1954).
6. T. Ojeda, D. Radić, L. Gargallo and D. Boys, *Makromol. Chem.*, **181**, 2237 (1978).
7. D. Radić, C. Dañin, A. Opazo and L. Gargallo, *Makromol. Chem. Symp.*, **58**, 209 (1992).
8. M. Yazdani-Pedram, L. Gargallo and D. Radić, *Eur. Polym. J.*, **21**, 461 (1985).
9. A. León, M. López, L. Gargallo, D. Radić and A. Horta, *J. Macromol. Sci.-Phys.*, **B(29)**, 351 (1990).
10. M. K. Neo and S. H. Goh, *Polym. Commun.*, **32**, 200 (1991).
11. S. M. Low, S. H. Goh, S. Y. Lee and M. K. Neo, *Polym. Bull.*, **32**, 187 (1994).
12. S. M. Low, S. Y. Lee and S. H. Goh, *Eur. Polym. J.*, **30**, 139 (1994).
13. M. Gordon and J. Taylor, *J. Appl. Chem.*, **2**, 493 (1952).
14. G. Belorgey and R. Prud'homme, *J. Polym. Sci., Polym. Phys.*, **20**, 191 (1982).
15. D. R. Paul and S. Newman, "Polymer Blends," Academic Press, New York, 1978.
16. D. S. Hubbel and S. L. Cooper, *J. Appl. Polym. Sci.*, **21**, 3035 (1977).
17. G. L. Brode and J. V. Koleske, *J. Macromol. Sci. Chem.*, **A-6**, 1109 (1972).
18. C. J. Ong and F. P. Price, *J. Polym. Sci., Polym. Symp.*, **63**, 59 (1978).
19. J. V. Koleske and R. D. Lundberg, *J. Polym. Sci.*, **A-2**, 765 (1969).