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# Properties of miscible blends of polyglutarimide with poly(styrene-co-maleic anhydride)

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In the present study, blends of styrene/maleic anhydride copolymer with polyglutarimide were studied using a variety of methods. The blends were found to be miscible over the entire composition range and showed positive deviations in glass transition temperature from the ideal (linear) behaviour. Fourier transform infra-red spectra of the blends showed the presence of significant interactions between the two polymers. These interactions were found to be possibly of a polar nature, involving the carbonyls of anhydride and imide rings respectively. Although the blends are miscible, synergism was not found for the mechanical properties of the prepared blends. The mechanical properties of the blends, however, showed additivity, as mechanical properties varied linearly with the composition. © 1997 Elsevier Science Ltd.

**(Keywords: polymer blends; polyglutarimide; polymer miscibility)**

## INTRODUCTION

Polyglutarimides (PGIs) are thermoplastic methacrylate-based copolymers which can be produced by reaction of poly(acrylic acid) or poly(methyl methacrylate) (PMMA) with amines or ammonia at 140–210°C for several hours. Commercial production of polymethacrylimides has been known since 1939[1]. In a later process[2] higher imidization levels (>95%) are achieved using an autoclave at higher temperatures and longer reaction times[3,4]. These reactions can also take place in a reactive extrusion process, usually in a twin screw extruder. In this case, imidization reaction can be completed within the residence time in the extruder[5–7]. The polymers produced exhibit high heat distortion temperatures, good mechanical and thermal properties, solvent resistance, improved dimensional stability and excellent optical properties. A variety of properties can be obtained by varying the pendant–NR alkyl group and the imidization levels. They are amorphous materials like PMMA, but they have higher glass transition temperatures ($T_g$s), due to the imide ring which is less flexible. The $T_g$ depends on the alkyl group of the primary amine and the degree of imidization. Generally, the $T_g$ increases as the alkyl group becomes shorter and bulkier and with increasing degree of imidization[4]. A commercial grade poly(*N*-methyl glutarimide)[8] (Rohm and Haas, KAMAX T-170) with a 90% degree of imidization has a $T_g$ of 168°C while for 100% imidization the $T_g$ rises to 184°C[4].

All these advantages make PGI copolymer materials suitable for a variety of uses, such as lithographic resists[9,10], glazing and lighting applications, packaging, medical devices, containers, gas barriers, adhesives, high rigidity foams and core materials for optical fibres[11].

Apart from uses in the pure form, PGI can also be used to improve the properties of other polymers by blending or grafting. PGI due to the unusual reactions that take place during their synthesis contain methacrylic anhydride, methacrylic acid and its salts as polymer units[12]. All these units can serve as sites for grafting reactions or molecular interactions (polar and hydrogen bonding). Recently polyamide/PGI graft copolymers have been synthesized by reactive extrusion of nylon 6 or nylon 6,6 and PGI in a twin screw extruder[13,14]. Polyamide–PGI ionomers have also been prepared in a similar way[15], giving materials with good toughness, optical clarity and gas barrier properties. PGI has also been blended with PVC[16], and polystyrene or styrene/[(meth)acrylonitrile] copolymers[17].

In the present study, it was decided to blend PGI with a styrene/maleic anhydride copolymer (SMA). The anhydride groups of SMA14 offer sites capable for polar or other interactions with the PGI macromolecules, thus increasing the possibilities for formation of miscible blends.

## EXPERIMENTAL

### *Materials*

In this study a random SMA copolymer was used, supplied by Arco Chemicals with trade name Dylark 332. The copolymer had $\bar{M}_W = 180\,000$ and contained 14 wt% maleic anhydride. Poly(*N*-methyl-glutarimide), with a trade name HT 510, was supplied from Rohm and Haas Co. It is a random copolymer containing methyl methacrylate and glutarimide units (1.47% N) and it will be referred to as PGI thereafter.

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Acetone used as solvent for the preparation of blends was of analytical grade (Aldrich).

### *Blends preparation*

Polyglutarimide was melt-blended with SMA14 in a Haake-Buchler Rheomixer model 600, with roller blades and a mixing head with a volumetric capacity of $69\,cm^3$. Prior to mixing the polymers were dried in a vacuum oven by heating at 80°C for 24 h, to prevent hydrolysis during the blend preparation at high temperatures. The components were physically premixed before being fed in the Rheomixer. Mixing was performed at 220°C and 60 rpm for a period of 30 min. The melt temperature and torque were continuously recorded during the mixing period on a Haake Rheocord, model 5000. A total of three samples were prepared, containing 25, 50 and 75 wt% of glutarimide respectively. The blends after preparation were immediately removed from the mixer, cooled to room temperature, milled and placed in tightly sealed vials to prevent any moisture absorption.

Blends of various compositions were also prepared by solution casting. Acetone solutions containing 10 wt% polymers were prepared and cast on aluminium dishes. Eight different blends were prepared containing 10, 25, 40, 50, 60, 75, 80 and 90 wt% SMA, respectively. The solvent was initially evaporated at ambient conditions. The final traces of solvent were removed by heating the blends under vacuum at 100°C for several days until weight constancy was achieved. The prepared polymer films had a thickness of approximately 150 $\mu$m.

### *Characterization*

Cloud point measurements were conducted on a Mettler FP82HT hot stage, controlled by a FP90 central processor unit. Polymer samples were placed on microscope glass slides and heated into the hot stage at temperatures higher than their $T_g$s. Afterwards, a cover glass was placed upon the samples and pressed to obtain a uniform polymer film. This procedure was necessary to obtain uniform thickness samples and to protect them from contact with air oxidation at the high temperatures used. An isothermal method was used for the determination of cloud points. Thus, each sample was heated at a certain temperature for 5 min, and was afterwards tested optically for any sign of opacity. The temperature was increased at regular increments of 20°C, starting from an initial temperature of 220°C, until phase separation was bracketed within two temperatures. Then the increment was decreased and the above procedure repeated starting from the lower temperature bound. The process stopped when the increment became less than 2°C.

This method, though more time consuming than the dynamical one (e.g. with a constant heating rate applied), permits a more accurate determination of the cloud point, especially when the turbidity develops very slowly. In this case, determination of cloud point with the dynamical method leads to a significant overestimation of the cloud point temperature.

Differential scanning calorimetry (d.s.c.) thermograms were recorded using a fast-quenching Shimadzu d.s.c. (model DSC-50Q), with indium as a calibration standard. About 8 mg from each sample was placed in a sealed aluminium cell. The samples were initially heated under a nitrogen atmosphere up to 200°C with a heating rate of $20°C\,min^{-1}$ in order to erase all previous thermal history, and subsequently they were immediately quenched. Each sample was rescanned under the same conditions, and from this second recording the $T_g$s were calculated.

Fourier transform infra-red (*FT*i.r.) spectra were acquired in a Biorad FTS-45A *FT*i.r. Spectrometer. For each spectrum 64 consecutive scans with $4\,cm^{-1}$ resolution were co-added. All spectral manipulations were done using the Win-IR$^{TM}$ software accompanying the instrument. Samples for *FT*i.r. measurements were prepared by solution casting of polymer solutions in acetone on KBr plates. The samples were dried overnight at 90°C under vacuum to remove all traces of solvent.

The microstructure of the blends was studied using the technique of scanning electron microscopy (SEM). Samples were fractured at liquid nitrogen temperatures and the surfaces were sputtered with gold. Measurements were performed on a Jeol model JSM-840A SEM.

Measurements of tensile strength were performed on an Instron mechanical tester, Model 1122, according to the ASTM D638 method. Measurements were done using a $5\,mm\,min^{-1}$ crosshead speed. Prior to measurements, the samples were conditioned at 50 ± 5% relative humidity for 24 h by placing them in a closed chamber containing a saturated $Ca(NO_3)_2{\cdot}4H_2O$ solution in distilled water (ASTM E-104). Five measurements were conducted for each sample, and the results were averaged to obtain a mean value.

Izod impact tests were performed on a Tinius Olsen instrument according to ASTM D256. The bars for impact tests were prepared by a hydraulic press at 220°C and 250 bar. Six measurements were conducted for each sample and the results averaged to obtain a mean value.

## RESULTS AND DISCUSSION

Mixing of the two polymers PGI and SMA, both by melt blending and by solution casting, gave perfectly transparent films for all mixture compositions. This fact alone suggests that the two polymers may be miscible. It is well known that immiscible polymers form opaque or translucent blends. However it is possible for two immiscible polymers to give transparent blends when they have very similar refractive indices. Thus, blend transparency is a strong indication, but not conclusive proof, of polymer miscibility. All blends, however, became opalescent upon heating at elevated temperatures, which is an indication of phase separation. This was confirmed by microscopic examination of the blends which revealed two phases. The cloud point curve of the blends is presented in *Figure 1*.

The cloud point curve has a parabolic shape, with a lower critical solution temperature (LCST) around 247°C at approximately 30 wt% SMA14 content.

### *Differential scanning calorimetry*

$T_g$ measurement is a valid method to establish polymer miscibility, since in miscible blends, only one $T_g$ appears at a temperature intermediate to that of the two pure polymers, which is composition dependent[18].

*Figure 2* shows the d.s.c. scan of a 50/50 PGI/SMA14 blend and of the pure polymers. It can be observed that only one $T_g$ exists, and it lies above $T_g$s of both pure polymers. This is more clearly visible in *Figure 3*, where the first derivatives of the above measurements are shown. Usually the single $T_g$ criterion applies only for polymers which differ more than 20°C in their $T_g$s. In our case this difference is less than 2°. However, the fact that

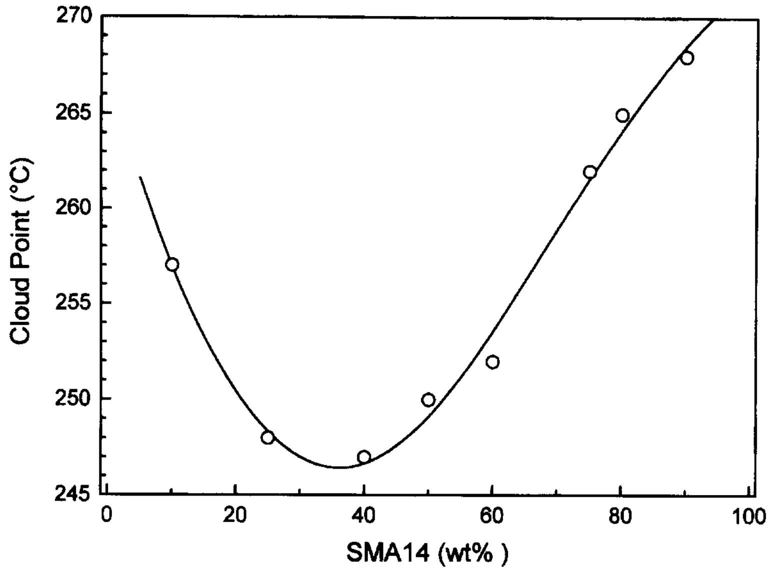

**Figure 1** Cloud points of SMA14/PGI blends

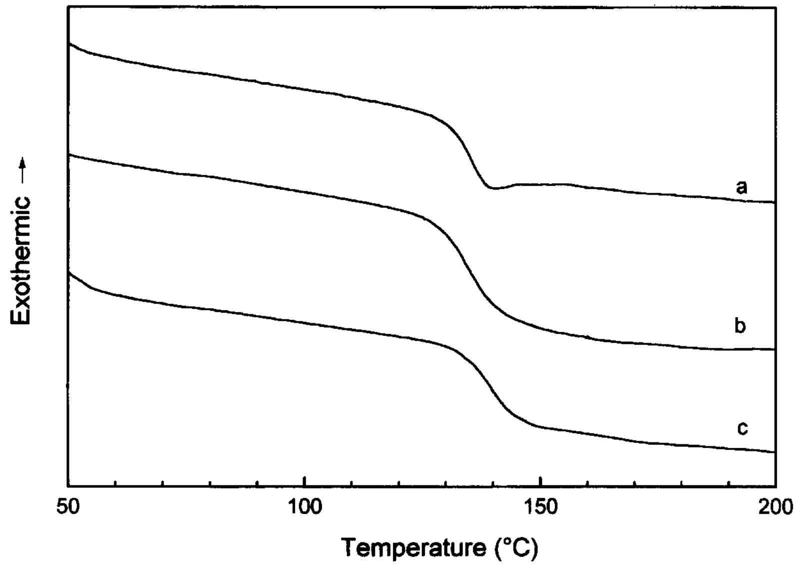

**Figure 2** D.s.c. scan of SMA14/PGI 50/50 blend and pure components: (a) SMA14; (b) PGI; (c) SMA/PGI 50/50 blend

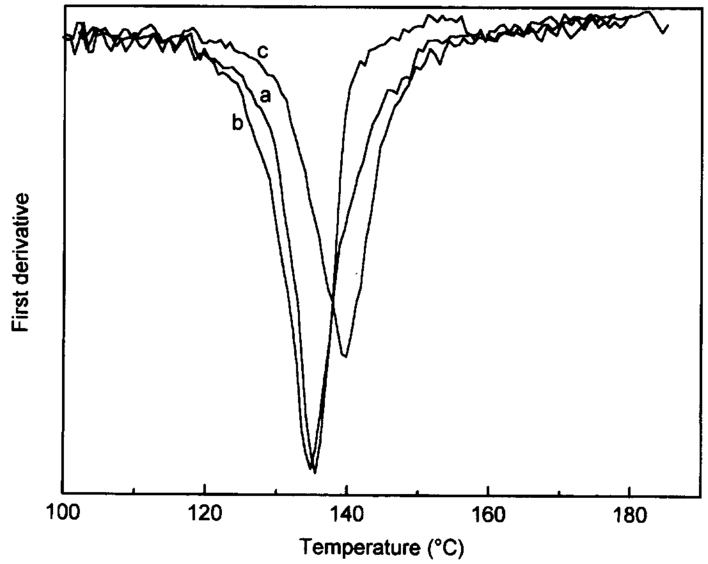

**Figure 3** First derivatives of the d.s.c. curves in *Figure 2* (lettering is the same as in *Figure 2*)

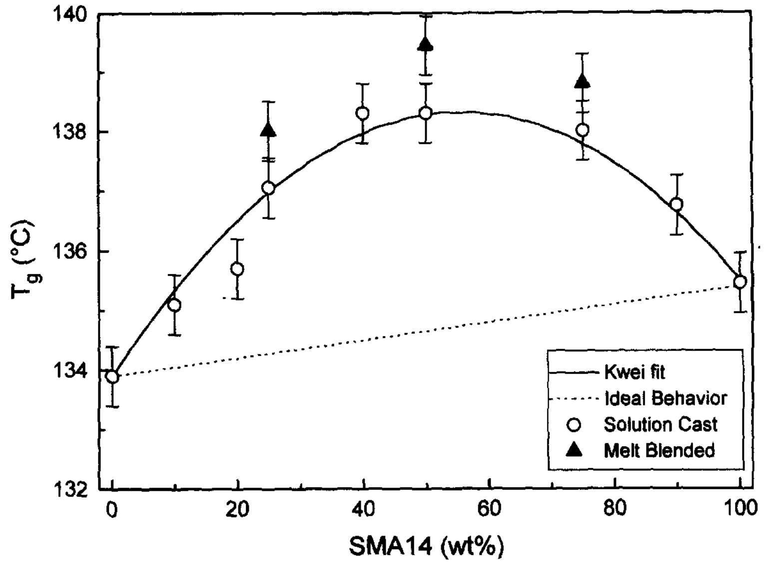

**Figure 4** $T_g$ vs blend composition diagram

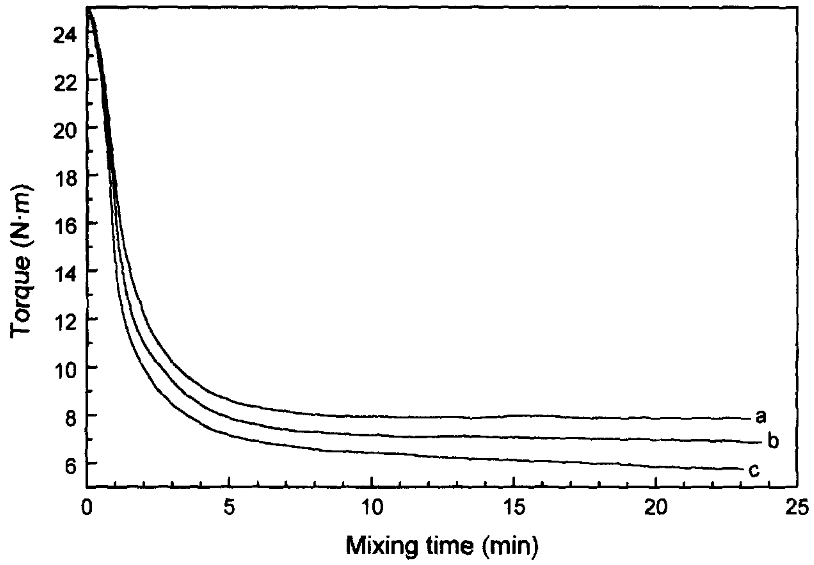

**Figure 5** Torque curves of SMA14/PGI blends prepared by melt blending: (a) 25/75 blend; (b) 50/50 blend; (c) 75/25 blend

the $T_g$ of the blend is higher than either of the two polymers suggests the formation of a new phase comprising both components.

A single glass transition temperature has been observed for all compositions in our blends prepared from melt or solution blending. The $T_g$ vs blend composition diagram is shown in *Figure 4*.

It can be observed that there is a positive deviation in $T_g$s for all blend compositions from the linear ('ideal') behaviour of the form $T_{gmix} = w_1 \cdot T_{g1} + w_2 \cdot T_{g2}$, where $w_i$ is the weight fraction of component $i$ in the blend. This deviation reaches a maximum near 50 wt% SMA. Such positive deviations are usual in miscible polymer blends, where strong interactions are present[19,20]. It is well known that $T_g$ depends on chain mobility, especially on segmental mobility. The increase in $T_g$ must be attributed to a decrease in the mobility of the polymer chain. This could happen either if crosslinked macromolecules are formed or very strong interchain interactions exist. In the second case the system behaves as a thermally reversible crosslinked network with the interactions serving as virtual crosslinks[21,22]. In polymer blends, where only non-polar (van der Waals) interactions exist, negative deviations from the linear behaviour are usually observed.

Crosslinked macromolecules can be produced when appropriate reactive groups exist in the blended polymers (reactive blending). In our case this could happen only if some of the imide rings were not closed and secondary amides ($-CO-NH-CH_3$) existed. These groups could react with the maleic anhydride units and give branched or crosslinked macromolecules. Should this happen however, an extended degree in branching would be necessary to cause such a large increase in $T_g$ (e.g. 5.6°C for the PGI/SMA14 50/50 blend). Torque measurements during melt mixing of the two polymers reveal no torque increase (*Figure 5*), as usually observed when a reaction occurs between the two components[23]. For example, it has been found that in reactive extrusion of PGI with polyamides there is a large increase in the melt viscosity of polyamide even for small amounts of added PGI[14].

As a rule, torque stabilizes after 15 min of mixing, and remains constant thereafter. It can be seen that melt viscosity increases with increasing glutarimide content. This must be attributed to the inherently higher melt viscosity of PGI, compared to that of SMA. The fact that no increase in torque is observed indicates that no chemical reaction takes place between the two polymers. Therefore the possibility of compatibility due to reaction between the two polymers (reactive compatibilization) must be rejected. Moreover, the increase in $T_g$, appears, also, in blends produced from acetone solution. Since solution mixing occurs under ambient temperature the possibility for reactions is reduced drastically and any observed miscibility is only due to thermodynamic reasons.

To ensure that no branched or crosslinked macromolecules were produced, extraction studies were performed upon the blends prepared by melt blending. It is well known that branched or crosslinked macromolecules are not soluble in common solvents at room temperature. Swelling is only observed in good solvents of the respective (linear) polymers. Acetone was used as an extraction solvent, since both PGI and SMA14 are soluble in acetone at room temperature. It was found that blends were completely soluble in acetone at room temperature and no swollen insoluble fraction was detected. All of the above indicate that no reaction takes place during mixing of SMA14 and PGI and that the positive deviations of the blends' $T_g$s are only due to interactions occurring between the two polymers.

Concerning the behaviour of the two types of blends, it can be observed that solution cast blends show lower glass transition temperatures compared to their melt blended counterparts of the same composition. This is probably due to traces of solvent remaining in the solution cast blends even after careful drying. It is well known that traces of solvents act as plasticizers, causing a depression in $T_g$. The second possibility that grafting or crosslinking reactions are taking place at the melt blended mixtures (which could cause an increase in the $T_g$ of the melt blended mixtures) has already been excluded.

T$_g$ *data correlation.* Several empirical or semi-empirical equations have previously been proposed, in order to correlate or predict the dependence of $T_g$ on the composition of the polymer blend. A recent development, based on the lattice–fluid hydrogen bonding (LFHB) theory is also available[24]. Application of this model requires the lattice–fluid scaling constants for the pure components. These constants for polyglutarimide are not yet available. Some classic and frequently employed equations include those proposed by Gordon and Taylor[25], Jenckel and Heusch[26], Fox[27], Couchman[28] Couchman and Karasz[29], Kwei[21] and Breckner *et al.*[30]. The first three can only account for negative deviations from the linear behaviour in the $T_g$–composition curves. The remaining two (Kwei and Breckner) can also predict positive deviations.

In our study, the equation of Kwei[21] was found to give the best fit of the $T_g$ data. This equation has the form:

$$T_g^{\text{blend}} = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} + q w_1 w_2$$

where $w_i$ and $T_{gi}$ are the weight fractions and the glass transition temperatures of the pure components, whereas $k$ and $q$ are adjustable empirical parameters. The $q$ value derived from the fit is a measure of the interaction strength. In our case we set $k = 1$, and only $q$ was used as an adjustable parameter. The best fit was obtained with a value of $q = 14.4$ and is represented as a solid line in *Figure 4*. The fit is very satisfactory, and all deviations from the theoretical line are well within experimental error, except from the value of the 20/80 blend. The relatively high value of the $q$ parameter indicates rather strong interactions between the components in the blends.

*Fourier transform infra-red spectroscopy*

*FT*i.r. is a method routinely used in polymer blends to establish the nature of interactions. In immiscible blends, the resulting spectrum is an almost perfect superposition of the two pure polymer spectra. On the contrary, miscible blends, where interactions develop between the two polymers, show significant changes in the intensities and/or frequencies of the peaks attributed to the interacting groups. As a result, after substraction of the pure component spectra from the blend, a significant residue remains, which constitutes the so-called 'interaction spectrum'.

*Figure 6* depicts the spectra for a 50/50 blend, the pure components and the resulting interaction spectrum. It can be seen that the interaction spectrum has a significant contribution in the overall blend spectrum. As pointed out by Allara[31], changes in the real part of refractive index of the blends, as compared to the pure components, could produce residual peaks in the subtraction spectrum due to dispersion effects. The magnitude of these peaks however is of the order of 1–2% of the initial intensities, whereas in our blends the residual peaks are much stronger.

The residual spectrum shows positive peaks at 1780, 1732, 1670 and 700 cm$^{-1}$. The peaks at 1780 and 700 cm$^{-1}$ are due to SMA14, and are attributed to anhydride carbonyl stretching and aromatic CH bending respectively. The other two peaks are due to PGI, and are characteristic of the amide and ester carbonyl stretching, respectively. The fact that these group vibrations appear in the interaction spectrum indicates that those groups are involved in the interaction between the two polymers. Thus, SMA14 interacts via the anhydride carbonyls and aromatic ring, whereas PGI with the imide carbonyls.

Interaction spectra of the other blends have a similar form and are presented in *Figure 7*. It can be seen that the interaction spectrum is fairly consistent throughout the composition range. Generally, the contribution of peaks due to SMA14 increases with increasing SMA14 content, with a concurrent decrease in the contributions of PGI peaks.

Factor analysis can be applied to polymer blends as a means of determining the number of components in a blend[32,33]. Some details about the method are given in the Appendix.

Generally, for an incompatible binary blend, only two factors appear, one for each pure component. In a miscible blend, however, additional factors emerge, representing the interaction between the components.

In our case, the data matrix subjected to factor analysis consisted of the *FT*i.r. spectra of eight blends measured at 701 frequencies within the 2000–650 cm$^{-1}$ region. Thus, the data matrix had dimensions of 701 × 8. Factor analysis of the data matrix are shown in *Table 1*.

No definite conclusion can be reached about the number of factors present, as there is no abrupt decrease

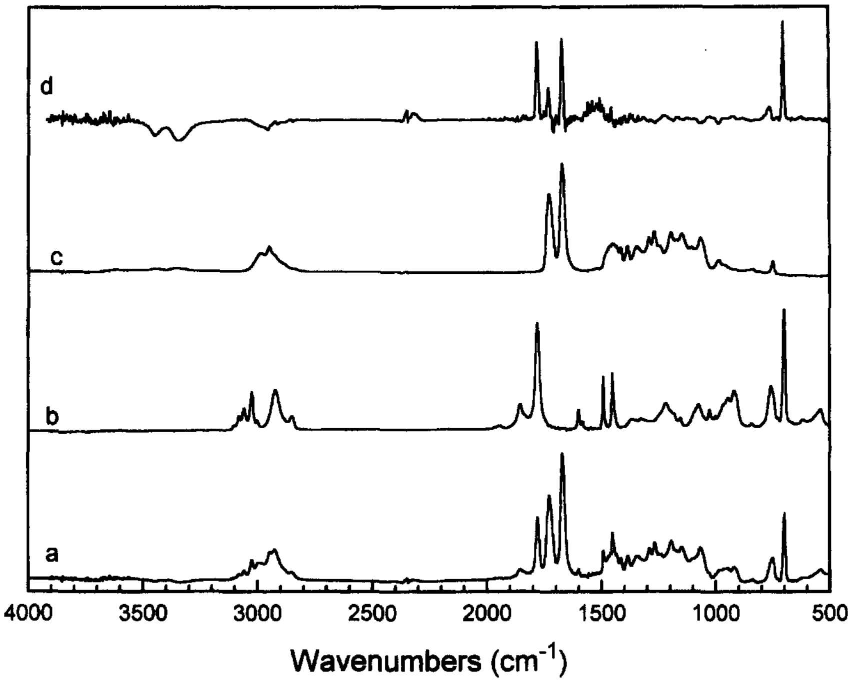

Figure 6 *FT*i.r. spectra of SMA14/PGI 50/50 blend: (a) SMA14/PGI 50/50 blend; (b) SMA14; (c) PGI; (d) interaction spectrum (magnified × 4)

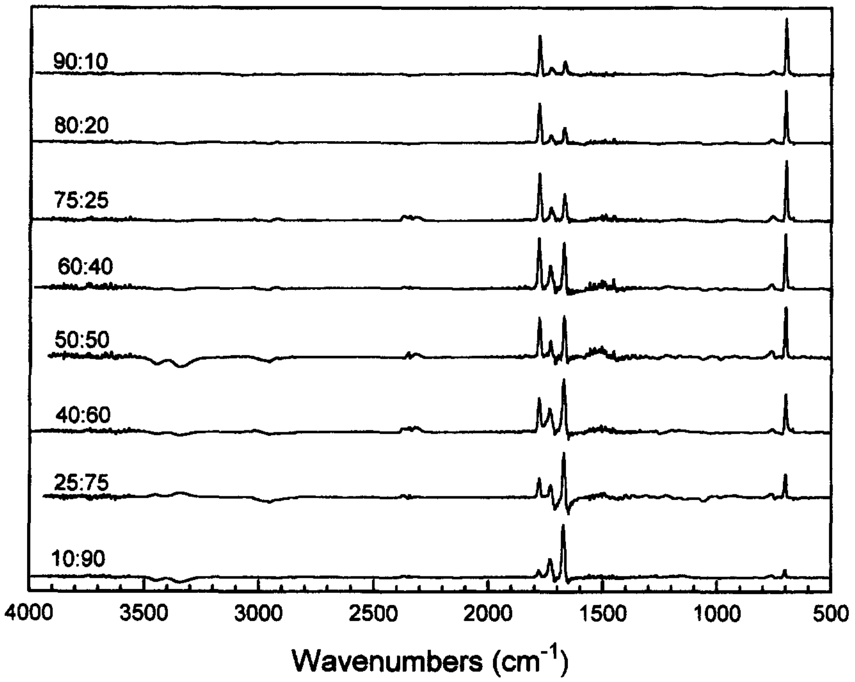

Figure 7 Interaction spectra of SMA14/PGI blends

Table 1 Factor analysis results for the *FT*i.r. data matrix

| $n$ | $\lambda_n$ | % Total |
|---|---|---|
| 1 | $2.861 \times 10^{-1}$ | 91.47 |
| 2 | $2.562 \times 10^{-2}$ | 99.66 |
| 3 | $8.152 \times 10^{-4}$ | 99.92 |
| 4 | $1.566 \times 10^{-4}$ | 99.97 |
| 5 | $4.853 \times 10^{-5}$ | 99.98 |
| 6 | $2.904 \times 10^{-5}$ | 99.99 |
| 7 | $1.189 \times 10^{-5}$ | 100.0 |
| 8 | $7.486 \times 10^{-6}$ | 100.0 |

in the magnitude of eigenvalues. This is usual when noise or background variations exist in the spectra. Malinowski's Indicator function[34], however, reaches a minimum at $n = 3$ as shown in *Figure 8*. Thus, we may conclude that three factors are present with the third additional factor arising from the interaction of the two polymers.

The exact nature of the interaction requires special consideration. Hydrogen bonding interactions are possible since PGI usually contains carboxyl moieties due to the unique mechanism of its synthesis, and possibly unfused imide rings. However, as can be seen in *Figure 9* showing the *FT*i.r. spectrum of PGI used, carboxyl peaks are absent and amide peaks are very weak in intensity. The absence of carboxyl groups may be the result of carboxyl end capping, which is a procedure routinely used in PGI polymers in order to minimize processing problems[35]. This end-capping reaction also eliminates anhydride groups. The final product of both reactions is a methyl methacrylate unit. Thus, the final

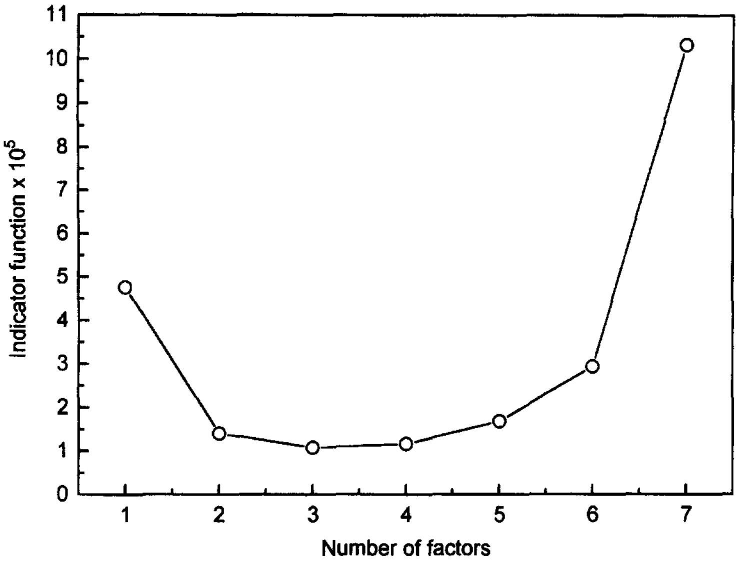

**Figure 8** Indicator function vs number of factors diagram

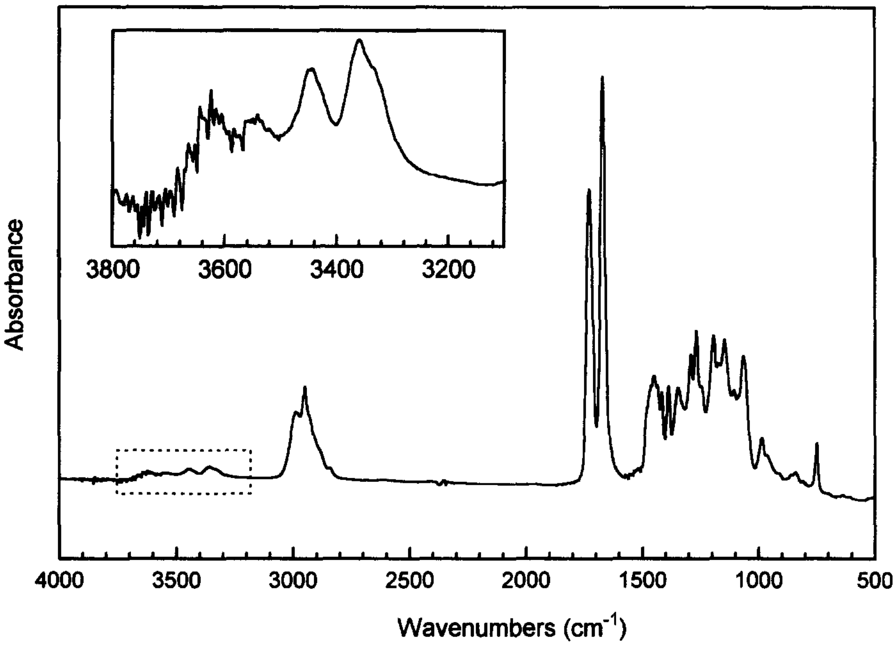

**Figure 9** *FT*i.r. spectrum of PGI (enlarged view of the 3800–3200 cm$^{-1}$ area shown in insert)

polymer is essentially a glutarimide/methyl methacrylate copolymer with only traces of carboxyl and anhydride groups present.

Moreover, the amide peaks appearing at 3444 and 3362 cm$^{-1}$ are very weak and broad. In fact, they may even not be amide peaks at all but carbonyl overtone peaks instead. This is substantiated by the fact that the relative intensity and frequency of these peaks does not change in the various blends. If they were amide peaks, there should be an increase in the peak at 3362 (bonded amide NH) with a concurrent decrease of the peak at 3444 cm$^{-1}$ when PGI was blended with SMA.

It seems that the concentration of hydrogen bonding groups in PGI is very low, and does not permit extensive hydrogen bonding between PGI and SMA. Neither the SMA, when examined by *FT*i.r., showed any presence of carboxyl groups due to anhydride hydrolysis. Thus, the overall contribution of hydrogen bonding to polymer miscibility is expected to be negligible.

Polar interactions are responsible for the miscibility of several polymer blends, such as, polystyrene/poly(vinyl methyl ether)[36] and polystyrene/poly(phenylene oxide)[37,38]. Miscibility in these blends is attributed to the formation of a complex between the ether oxygen and the benzene ring of styrene. Most interestingly, the positive peak appearing at 700 cm$^{-1}$ in the interaction spectrum is characteristic of the benzene ring. Thus, there is a possibility of such an interaction in our blends. To test this assumption, a 50/50 blend of polystyrene (replacing SMA) and PGI was prepared by solution casting from a THF solution. In this blend, the polar anhydride groups are absent and the only possible interactions are through the styrene ring. This blend, however, gave opaque films and had two $T_g$s as shown in *Figure 10*.

Thus, it seems that those interactions are rather weak (at least in PS/PGI blends) and cannot effect miscibility. It must be noted however, that the styrene units in SMA copolymers are in a characteristically

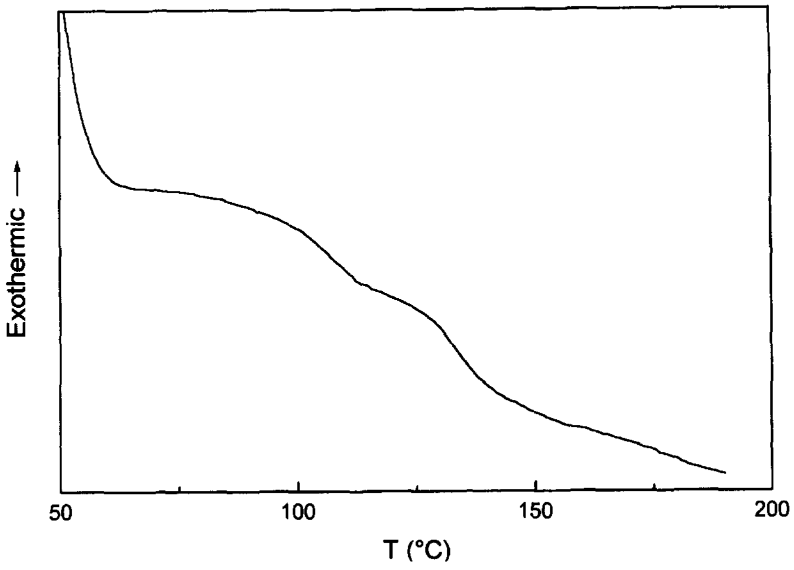

Figure 10 D.s.c. thermogram of a PS/PGI 50/50 blend

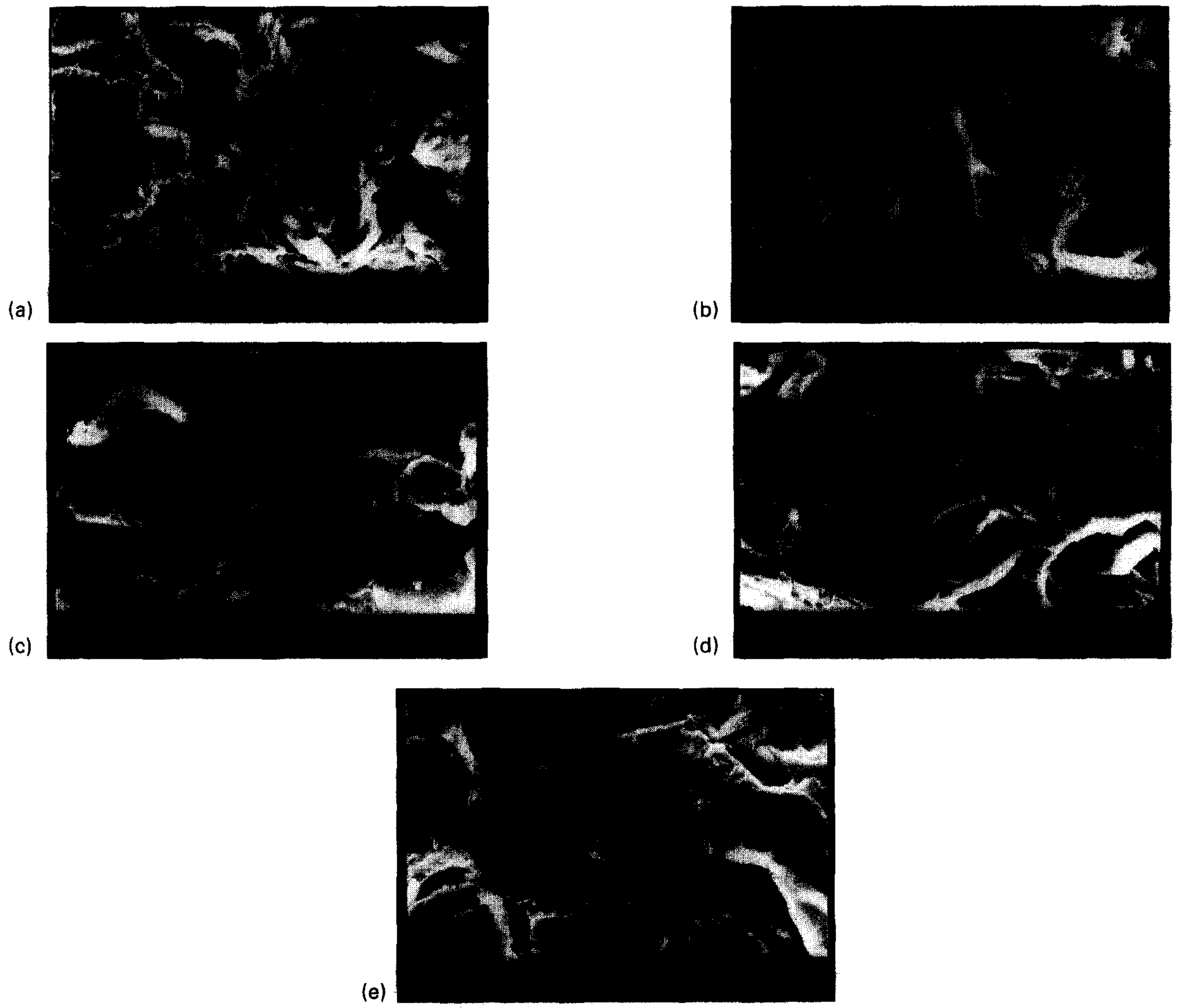

Figure 11 SEM micrographs of cryogenically fractured surfaces of pure PGI (a), pure SMA14 (b) and PGI/SMA14 blends: 25/75 (c), 50/50 (d) and 75/25 wt% (e)

different environment. The SMA system is a classic example of monomers which have a high tendency to give alternating copolymers. In these copolymers most of the styrene units are placed between two electron withdrawing maleic anhydride units. This results in a lower electronic density of the aromatic ring, and enhances its character as an electron acceptor. Since the imide nitrogen of PGI is an $n$-electron donor, an interaction between it and the aromatic ring is possible. Such electron donor–acceptor complexes formed in blends have been reported

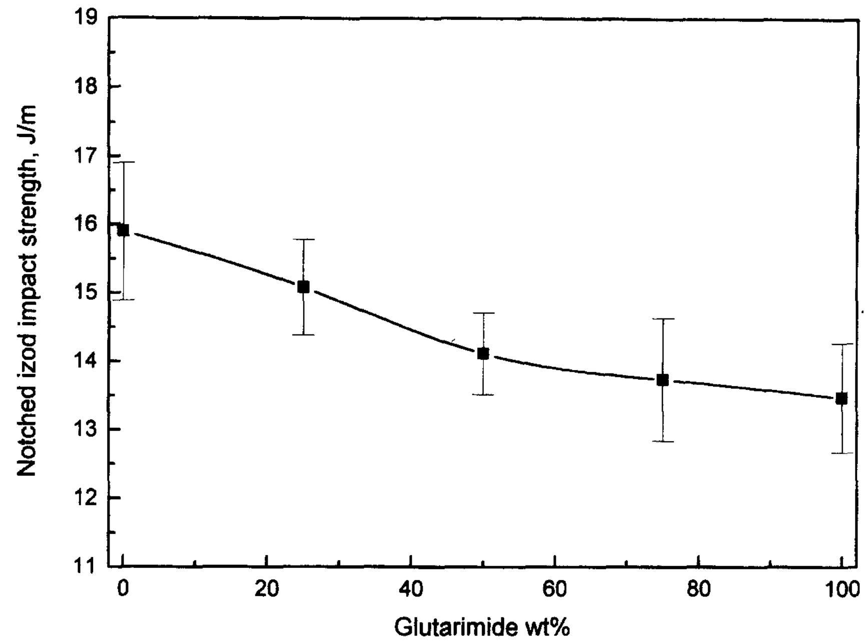

**Figure 12** Impact strength of PGI, SMA14 and their blends

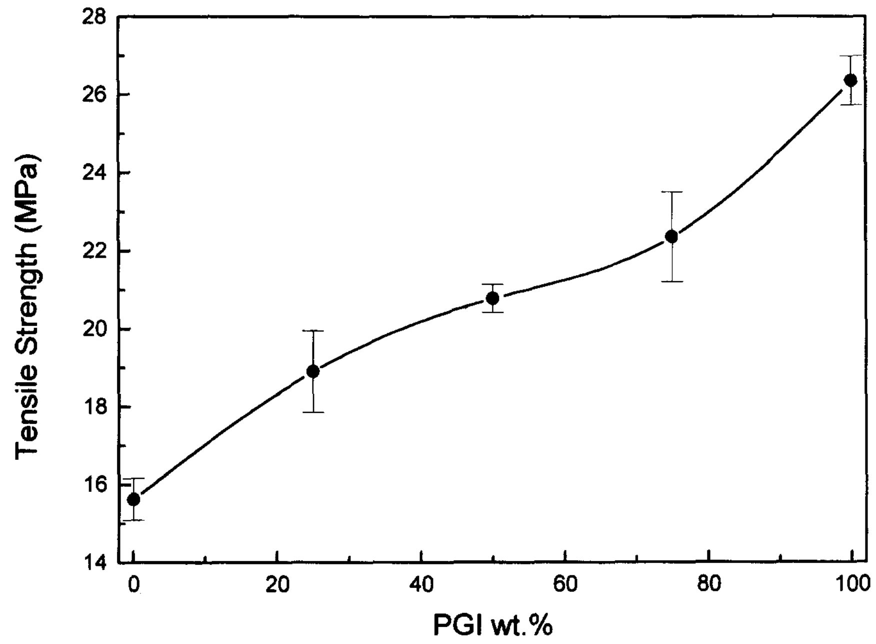

**Figure 13** Tensile strength of PGI, SMA14 and their blends

in the literature[19]. Thus, it seems that the interactions occurring are of a polar nature and are developed mainly between the imide and anhydride aromatic rings of PGI and SMA14 respectively.

### *Blend morphology*

SEM is a useful technique for studying the distribution of the component phases in immiscible polymer blends. It is not very useful when the blends are miscible. It can be used, however, for excluding colloidal size phase separation[39]. Typical morphology of cryogenically fractured surfaces of our blends are shown in *Figure 11*.

As can be seen, there is only one phase for the entire composition range of the blends. The surfaces are similar to those of the pure components (*Figure 11*), and this is further evidence that the two polymers do not phase-separate in this microscale.

### *Mechanical properties*

In immiscible blend systems, the thermomechanical behaviour is strongly influenced from the interfacial characteristics and the size distribution of the component phases[40]. Since in our blends only one phase is detected, it is expected that the mechanical properties range in a regular manner between those of the two pure components.

The variation with composition of the impact strength of our blends with composition is presented in *Figure 12*. The two polymers have similar impact strengths, with SMA14 having impact strength about 3.5 J m$^{-1}$ higher than PGI. In their blends, the impact strength lies between those of the two pure polymers. The impact strength of the blends decreases monotonically with increasing amount of PGI. The opposite trend is observed in tensile strength. SMA14 has a lower tensile strength than PGI, and as can be seen in *Figure 13*, the tensile strength of the blends, varies smoothly with polymer composition. It increases almost linearly with increasing PGI content with no synergism or antagonism.

## CONCLUSIONS

The optical, spectroscopic, thermoanalytical, and mechanical experimental evidence provided by the present work confirms the miscibility of the system SMA/PGI over the entire composition range. The system exhibits a smooth cloud point curve and a lower critical solution temperature of 247°C at approximately 30 wt% SMA14 content. A rather strong positive deviation from linearity is observed in the variation with blend composition of the glass transition. The nature of the interactions responsible for the miscibility seem to be the polar interactions between the imide and anhydride aromatic rings of PGI and SMA14 respectively. Hydrogen bonding interactions have been excluded, or are of minor importance. Reactive blending and extensive crosslinking have also been excluded.

## REFERENCES

1. Graves, G., US Patent No. 2146209, 1939.
2. Schroederand, G. and Tessmar, K., US Patent No. 3284425, 1966.
3. Patterson, J. R. and Gruder, C. M., *J. Vinyl Tech.*, 1988, **10**, 158.
4. Choi, H. W., Lee, Y. C., Kim, B. J., Won, H. Y., Kim, Y. S. and Chin, I., *Proc. Am. Chem. Soc. PMSE*, 1995, **72**, 357.
5. Kopchik, R. M., *Ger. Offen.*, 2652118, 1977.
6. Kopchik, R. M., US Patent No. 4246374, 1981.
7. Tzoganakis, C., *Adv. Polym. Tech.*, 1989, **9**, 321.
8. Rohm and Haas, *KAMAX*™, Resins Technical notes, Philadelphia, Pa., 1990.
9. Hiraoka, H., Gipstein, E., Bargon, J. and Welsh, L. W., *J. Appl. Polym. Sci.*, 1978, **22**, 3397.
10. Bargon, J., Gipstein, E. and Hiraoka, H., US Patent No. 3964908, 1976.
11. Wright, W. W. and Hallden-Abberton, M., in *Ullman's Encyclopedia, Polyimides*, Vol. A21. VCH, Weinheim, 1992.
12. Hallden-Abberton, M., *Polym. Mater Sci. Eng.*, 1991, **65**, 361.
13. Hallden-Abberton, M., *Proc. Am. Chem. Soc. PMSE*, 1993, **68**, 245.
14. Hallden-Abberton, M., *Proc. Am. Chem. Soc. PMSE*, 1993, **68**, 249.
15. Hallden-Abberton, M. and Paul, M., Eur. Patent No. 409481, 1991.
16. Kopchik, R. M., US Patent No. 4255322, 1981.
17. Henry, W., Eur. Patent No. 95274, 1983.
18. Utraki, L., in *Polymer Blends and Alloys*. Hansen, New York, 1989.
19. Rodriquez-Parada, J. M. and Percec, V., *Macromolecules*, 1986, **19**, 55.
20. Lu, X. and Weiss, R. A., *Proc. Am. Chem. Soc. PMSE*, 1991, **64**, 163.
21. Kwei, T. K., *J. Polym. Sci., Polym. Letts Edn*, 1984, **22**, 307.
22. Pearce, E. M., Kwei, T. K. and Min, B. Y., *J. Macromol. Sci., Chem.*, 1984, **20**, 191.
23. Tselios, C., Bikiaris, D., Prinos, J. and Panayiotou, C., *J. Appl. Polym. Sci.*, in press.
24. Prinos, J. and Panayiotou, C., *Polymer*, 1995, **36**, 1223.
25. Gordon, M. and Taylor, J. S., *J. Appl. Chem.*, 1952, **2**, 495.
26. Jenckel, F. and Heusch, R., *Kolloid Z.*, 1953, **30**, 89.
27. Fox, T. G., *Bull. Am. Phys. Soc.*, 1956, **1**, 123.
28. Couchman, P. R. and Karasz, F. E., *Macromolecules*, 1978, **11**, 117.
29. Couchman, P. R., *Macromolecules*, 1978, **11**, 1156.
30. Brekner, M. J., Schneider, H. A. and Cantow, H. J., *Polymer*, 1988, **29**, 78.
31. Allara, D. L., *Appl. Spectrosc.*, 1979, **33**, 358.
32. Malinowski, E. R., *Anal. Chem.*, 1977, **49**, 607.
33. Koenig, J. L., in *Spectroscopy of Polymers*, ASC Professional Reference Book. ACS, Washington DC, 1992, p. 93.
34. Malinowski, E. R., *Anal. Chem.*, 1977, **49**, 612.
35. Hallden-Abberton, M., Bortnick, N., Cohen, L., Freed, W. and Fromuth, H., US Patent No. 4727117, 1988.
36. Garcia, D., *J. Polym. Sci., Polym. Phys. Edn*, 1984, **22**, 107.
37. Wellinghoff, S. T., Koening, J. L. and Baer, E., *J. Polym. Sci., Polym. Phys. Edn*, 1977, **15**, 1913.
38. Koening, J. L. and Tovar Rodriquez, M. J. M., *Appl. Spectrosc.*, 1981, **35**, 543.
39. Fekete, E., Pukanszky, B. and Peredy, Z., *Angew. Makromol. Chem.*, 1992, **199**, 87.
40. Barlow, J. W. and Paul, D. R., *Polym. Eng. Sci.*, 1984, **24**, 525.

## APPENDIX

### *Factor analysis basics*

Factor analysis is a multivariate data analysis technique first applied in behavioral sciences studies, but has gained widespread acceptance in other scientific disciplines as well.

Factor analysis is based on the diagonalization of the covariance matrix Z[32]:

$$Z = A^{T}A$$

where $A$ is a $r \times c$ data matrix consisting of $r$ variables measured for $c$ samples.

The diagonalization of the $Z$ matrix produces a set of eigenvalues $\lambda_i$ ($i = 1, 2, \dots, c$) and associated eigenvectors $v_i$ arranged in descending order. Each eigenvector corresponds to a factor, and the magnitude of its eigenvalue is a measure of the factor's importance in reconstructing the initial data.

The factors can be separated into two groups; one group of factors has large eigenvalues and is associated with real data, and a secondary group of factors has much lower eigenvalues and is associated only with noise. Thus, only a subset of $n$ factors is necessary to successfully represent the data. The deduction of the number of significant factors $n$ is a non-trivial process, especially for noisy data, however a large drop is usually observed between the $n$ and $n + 1$ eigenvalue with remaining eigenvalues dropping more slowly. Koenig has suggested the determination of the number of factors by a visual inspection of the log ($\lambda$) vs factor number plot[33].