Solid state ^{13}C n.m.r. detection of molecular mixing in polymer blends that exhibit multiple eutectic phase transformations

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Blends of poly(ethylene oxide) with various isomers and derivatives of dihydroxybenzene generate rich macroscopic phase behaviour characterized by solid–solid–liquid (eutectic) transformations. These phase transitions, which occur above ambient temperature, are measured directly by d.s.c., and a thermal analysis summary is contained in the temperature–composition projections. The work described here focuses on site-specific interactions at the molecular level that are responsible for this unique phase behaviour. Solid state n.m.r. spectroscopy is useful as a diagnostic probe of strong interactions and crystal structure modifications. The isotropic ^{13}C chemical shift detects phase coexistence at temperatures well below the eutectic and liquidus transitions where the d.s.c. thermograms are featureless. I.r.-detectable hydrogen bonds between the ether oxygen of poly(ethylene oxide) and the hydroxyl protons in either hydroquinone, 2-methylresorcinol or 5-methylresorcinol distort electron density within the π-orbitals of the aromatic ring. Consequently, the aromatic carbon n.m.r. signals of the resorcinol-like small molecules are sensitive to hydrogen bonding and the formation of molecular complexes. Multiple signals are observed for chemically equivalent carbon sites in the small molecules when phase coexistence is favoured. Crystal structure considerations and molecular packing within the unit cell also generate ^{13}C chemical shift multiplicities, illustrated here for undiluted hydroquinone. The correlation between phase behaviour and ^{13}C n.m.r. diagnostics provides a phenomenological interpretation of the spectroscopic results, particularly for trieutectic blends of poly(ethylene oxide) with 2-methylresorcinol. The combination of n.m.r. and thermal analysis allows high-temperature d.s.c.-measured phase boundaries to be extrapolated to lower temperatures dictated by the n.m.r. experiment.

(Keywords: ^{13}C n.m.r.; molecular mixing; blends; eutectic phase transformations)

INTRODUCTION

Solid state ^{13}C n.m.r. spectroscopy is employed in this study as a site-specific diagnostic probe of molecular complexation and phase behaviour of three poly(ethylene oxide) (PEO)/small molecule blends that exhibit eutectic phase transformations. In each system investigated, precipitation from aqueous solution produces a molecular complex with a crystal lattice structure that is distinguishable spectroscopically from the undiluted small molecule. In previous studies carried out in this laboratory, d.s.c. was used to generate temperature–composition phase diagrams for methanol-cast blends of PEO with various isomers and derivatives of dihydroxybenzene[1–4]. Concentration-dependent melting is observed over the entire composition range in each case. The results are rather unique from the viewpoint of polymeric phase behaviour because multiple eutectic transitions are present, separated by homogeneous solid solutions that contain a prescribed 'integer ratio' of interacting functional groups.

N.m.r. chemical shifts and linewidths are sensitive to molecular symmetry and long-range periodicity that is characteristic of the crystallographic unit cell. This concept is demonstrated by the successful correlation of polyester carbonyl n.m.r. chemical shifts and linewidths with crystallinity and molecular mobility in blends of main-chain polyesters with poly(vinyl phenol) (PVP)[5]. The electronic distribution in the vicinity of a critical ^{13}C site is measured indirectly by the chemical shift tensor, and molecular mixing in *strongly interacting* systems is sufficient to distort electronic wavefunctions and isotropic chemical shifts. The phenolic carbon resonance of resorcinol[1,2] and its polymeric analogue PVP[6] has been correlated with much success to macroscopic phase behaviour in blends with PEO. A critical interaction site, such as the aromatic COH of resorcinol, is defined as one that is sensitive to crystallographic symmetry of the unit cell and microenvironmental aspects of mixing. A critical component can detect one or more coexisting phases via chemical shifts that differ because crystal structure and molecular conformations are affected by the blending process.

Several examples from the literature provide evidence that eutectic phase behaviour is not uncommon in polymer/small molecule blends. Smith and Pennings *et al.* reported that the following binaries produce one eutectic transition line in the temperature–composition phase diagram: polyethylene with 1,2,4,5-

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tetrachlorobenzene[7]; polyethylene with hexamethylbenzene[8]; isotactic polypropylene with 1,2,4,5-tetrachlorobenzene[9]; and isotactic polypropylene with pentaerythrityl tetrabromide[10]. The ternary system polyethylene/hexamethylbenzene/adamantane exhibits one eutectic transformation that is best illustrated in a variety of binary projections of the ternary phase diagram[11]. All five examples mentioned above[7–11] contain, at most, only one polar component and, hence, cannot be classified as strongly interacting systems. In this respect, one concludes that strong interaction between dissimilar components is not required for a system to exhibit single eutectic response. Wittmann and St. John Manley identified single eutectic phase behaviour in blends of polycaprolactone with trioxane[12], and PEO with trioxane[13]. In these examples both components contain polar moieties but acid–base interactions are not favourable. When acid–base effects do have the potential to play a major role in solid state phase behaviour, Gryte *et al.* reported eutectic response for PEO and glutaric acid[14] but, once again, only one solid–solid–liquid transition was observed. One of the classic textbook examples of bieutectic response is provided by Adamson for the *p*-toluidine/phenol binary[15]. In this case, a homogeneous intermediate solid solution (i.e. molecular complex or the so-called 'line compound') separates two eutectic transition lines when the interacting functional groups in the dissimilar components (i.e. –OH and $-NH_2$) are present in equimolar concentrations.

The small molecules chosen for investigation here represent isomers or derivatives of resorcinol (dihydroxybenzene). Resorcinol *versus* hydroquinone allows one to study the effect of aromatic hydroxyl group placement in the *meta* and *para* positions on the potential for hydrogen bonds to form with the ether oxygen of PEO. The temperature–composition phase diagram of hydroquinone and PEO illustrated in *Figure 1* exhibits two eutectic transformations at the same temperatures as those found in the PEO–resorcinol system[1]. Interestingly enough, one of the solid–solid–liquid (eutectic) transition lines in the PEO–hydroquinone phase diagram (at ~80°C) represents the classic crossover between eutectic and peritectic transformations[16,31,32]. 2-Methylresorcinol and 5-methylresorcinol allow one to probe aromatic substituent effects due to a methyl group. Furthermore, 2-methylresorcinol also introduces a steric effect because the methyl group is *ortho* to both hydroxyls and, hence, is extremely close to any macromolecular chain that preferentially forms hydrogen bonds with both hydroxyl protons in the same small molecule. The PEO/5-methylresorcinol system exhibits two eutectic phase transformations, and the PEO/2-methylresorcinol phase diagram boasts three eutectics as illustrated in *Figure 2*. A binary system that exhibits three eutectic phase transformations necessarily forms two molecular complexes (i.e. homogeneous solid solutions β and γ that contain an appreciable amount of both components). This is extremely rare for both large and small molecule mixtures.

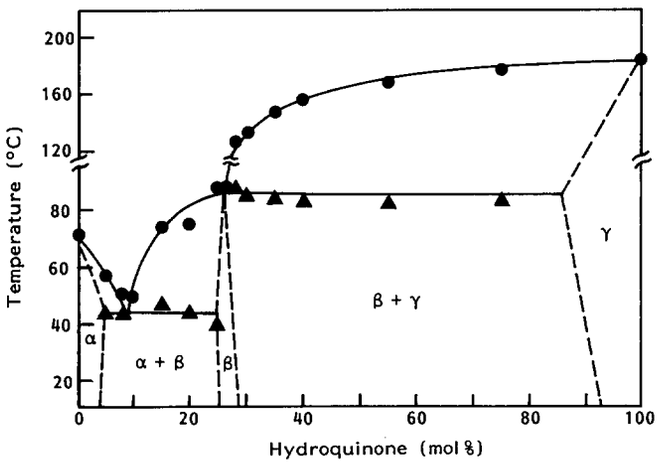

Figure 1 Temperature–composition projection of the binary phase digram for methanol-cast blends of PEO ($M_w = 900\,000$) and hydroquinone. D.s.c. thermograms were used to construct the eutectic (▲) and liquidus (●) phase boundaries. The thermograms were recorded at a heating rate of 5°C min^{-1} for most blend compositions. In some cases, a heating rate of 0.25°C min^{-1} was used to resolve the eutectic and liquidus melting transitions

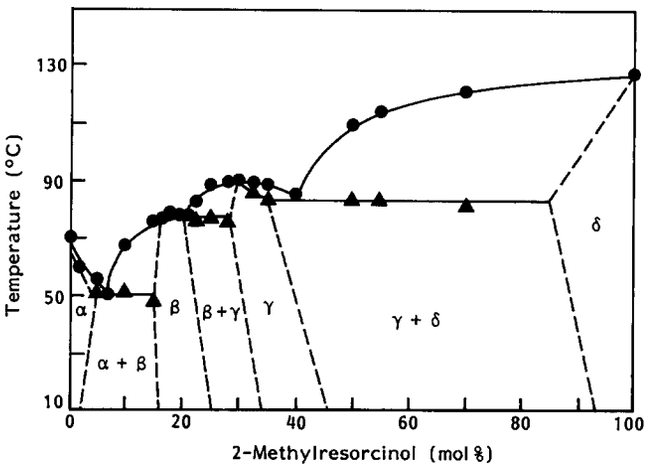

Figure 2 Temperature–composition projection of the binary phase diagram for methanol-cast blends of PEO ($M_w = 900\,000$) and 2-methylresorcinol. D.s.c. thermograms were used to construct the eutectic (▲) and liquidus (●) phase boundaries, and n.m.r. data for the C5 aromatic carbon were employed to extrapolate the solid–solid phase boundaries (– – –) to ambient temperature and below. The thermograms were recorded at a heating rate of 5°C min^{-1} for most blend compositions. In some cases, a heating rate of 0.25°C min^{-1} was used to resolve the eutectic and liquidus melting transitons

EXPERIMENTAL

Materials and sample preparation. High molecular weight PEO ($M_w = 900\,000$) was purchased from Scientific Polymer Products, and hydroquinone, 2-methylresorcinol and 5-methylresorcinol (orcinol monohydrate) were purchased from Aldrich Chemical Company. All materials were used as received. Physical mixtures were prepared from dilute methanol solutions (0.05 g solid ml^{-1}) at 35°C. Upon evaporation of the solvent in a fume hood, the residues of each polymer blend were dried under vacuum at ambient temperature for ~12 h, followed by compression moulding at the melting temperature of the undiluted small molecule for ~1–2 min with subsequent slow cooling to room temperature. This procedure produced acceptable homogeneous films when the polymer blend residues from solution evaporation appeared to be macroscopically phase separated. All homogeneous films were annealed in a vacuum dessicator for 2 weeks at room temperature before physical characterization was attempted. Blend composition was controlled by accurately weighing the starting materials before dissolution in methanol. Thermogravimetric analysis of the solid residues

yielded mixture compositions that were within 2% of the weights of the starting materials. An alternate route to produce blends of PEO with each isomer or derivative of dihydroxybenzene relies on the driving force for complexes to form via precipitation from aqueous solution[17]. Each pure component is soluble in distilled water. However, when aqueous solutions of the pure components are mixed at 50–60°C, the formation of a colourful precipitate suggests that (i) unusual interactions are operative in addition to hydrogen bonding, and (ii) the overall mixture composition lies within a two-phase region of the ternary aqueous phase diagram. The latter concept has been illustrated by Gashgari and Frank[18] for ternary mixtures of two high molecular weight polymers in toluene. It should be mentioned that the precipitation method produces hydrogen-bonded complexes whose compositions are difficult to control because the starting materials are partitioned between the precipitate and the supernatant solution in unpredictable proportions (unless one has detailed information about the ternary phase diagram of PEO, dihydroxybenzene isomer or derivative, and water). Hence, it is not possible to span a wide range of blend concentrations via the precipitation method. In this respect, only one blend is discussed that portrays the characteristics of the precipitate from aqueous solution. Methanol-cast blends without precipitate formation were employed to construct the temperature–composition projection of the phase diagram via thermal analysis.

Solid state ^{13}C n.m.r. spectroscopy. Proton-enhanced dipolar-decoupled solid state ^{13}C n.m.r. spectra were obtained on a modified Nicolet NT-150 spectrometer at the NSF-supported Regional NMR Center, Colorado State University, Fort Collins, Colorado. The carbon frequency was 37.735 MHz and magic angle spinning was performed at 3600 Hz. The spectrometer incorporates a double-resonance cross-polarization/magic angle spinning probe that was designed and constructed at the CSU Regional NMR Center. The spinner system is a modified version of that of Wind *et al.*[19] with a sample volume of 0.3 cm^3. A proton 90° pulse width of 5 μs was employed, corresponding to an r.f. field strength of 50 kHz. The r.f. field was maintained at 50 kHz during cross-polarization and subsequent high-power ^1H decoupling. The ^{13}C free induction decay (f.i.d.) was accumulated in a 2 K time-domain window using quadrature detection. Prior to Fourier transformation, the signal-averaged f.i.d. was zero-filled to 4 K. The spectral width encompassed a ± 10 kHz frequency range and 5–10 Hz of line broadening was employed. Following Stejskal and Schaefer[20], spin-temperature alternation in the rotating frame was used to suppress the build-up of artifacts which may occur in proton-enhanced spectra. The sample temperature was maintained at 15 ± 2°C by passing the spinner air through a copper cooling coil immersed in an ice bath. ^{13}C chemical shifts were referenced externally to the methyl resonance of hexamethylbenzene, 17.355 ppm deshielded from tetramethylsilane[21].

Differential scanning calorimetry. Thermal analysis was performed on a Perkin-Elmer DSC-7 with the overall goal of generating temperature–composition phase diagrams. Melting endotherms were recorded under helium and nitrogen purges during the first heating trace *in the calorimeter*. Heating rates between 0.25°C min^{-1} and 5°C min^{-1} were employed, the former being necessary in some blends to resolve eutectic and liquidus melting peaks. Differential power output was monitored via Perkin Elmer's TAC 7/DX thermal analysis controller in conjunction with the DSC7 multitasking software on a 386/33 personal computer. Following the suggestions of Etter *et al.*[22] and Gutt and Majumdar[23], eutectic and liquidus transition lines in the temperature–composition projection of the phase diagram were constructed based on the following interpretation of the d.s.c. melting endotherms. When eutectic melting occurs, either in eutectic or off-eutectic mixtures, the peak temperature of the relatively sharp endotherm is used to construct a concentration-independent isothermal phase boundary representing three-phase (solid–solid–liquid) equilibria. The eutectic phase boundary separates the solid–solid two-phase region from (i) the homogeneous isotropic liquid state at the eutectic composition, and (ii) the solid–liquid two-phase regions for off-eutectic mixtures. When concentration-dependent melting occurs over a rather broad temperature range above the eutectic endotherm in off-eutectic mixtures, the endpoint of this broad asymmetric melting event is used to construct the liquidus phase boundary which separates the solid–liquid two-phase regions from the homogeneous isotropic liquid state. When congruent melting occurs at local maxima on the liquidus line corresponding to the pure components or the intermediate homogeneous solid solutions (i.e. molecular complexes), the endpoint of the relatively sharp endothermic transition is chosen.

RESULTS AND DISCUSSION

Bieutectic mixtures of PEO with hydroquinone

Hydroquinone dissolves completely in distilled water, and a clear solution is obtained with moderate stirring action. When aqueous solutions of hydroquinone and PEO are mixed, the ternary system is initially yellow and slowly turns dark red. The precipitate that forms is also dark red. This precipitate dissolves rather easily in freshly distilled water suggesting that the equilibrium supernatant contains dissolved solids. Over the course of a few days, the initial precipitate also redissolves in the original supernatant solution. Centrifugation and vacuum drying of the aqueous precipitate were performed to obtain a solid complex of PEO and hydroquinone that did not contain measurable amounts of water. The weight of the dried precipitate was monitored until the mass was constant to within ± 0.5 mg.

Solid state ^{13}C n.m.r. signals of hydroquinone in its undiluted crystalline state and the precipitate with PEO are illustrated in *Figure 3*. The phenolic carbons of hydroquinone are observed in the chemical shift range from 146 to 151 ppm, and they appear as a series of three crystallographically inequivalent resonances in the undiluted state. Five signals between 115 ppm and 121 ppm in *Figure 3A* represent the protonated aromatic carbons of undiluted hydroquinone, and four of these signals are well resolved. Hydroquinone crystallizes in three modifications, designated α, β and γ[24–28]. The trigonal/hexagonal α-modification is most stable at room temperature with 54 molecules in each unit cell of hexagonal dimensions, and three molecules in each asymmetric unit[26]. The ^{13}C n.m.r. data in *Figures 3–5*

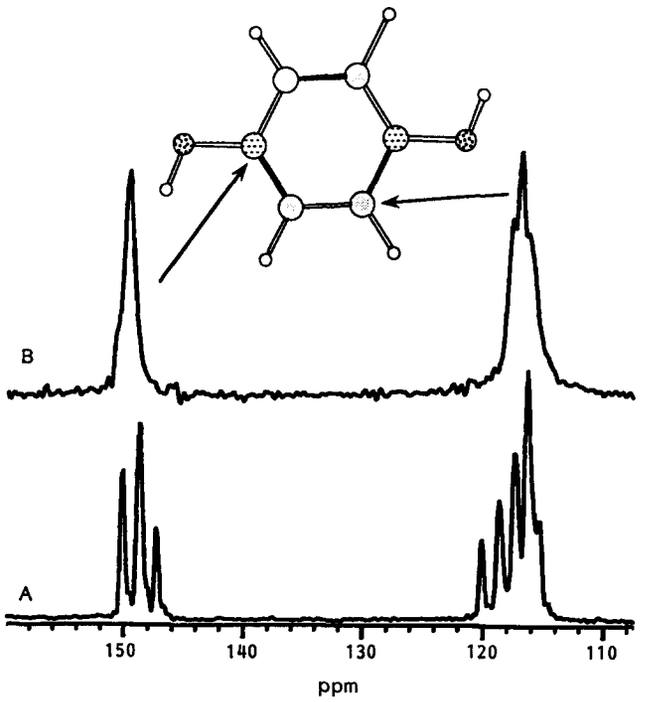

Figure 3 High-resolution solid state ^{13}C n.m.r. signals of hydroquinone in the undiluted crystalline state (A, 60 s pulse repetition delay) and in an aqueous precipitate with PEO (B, 2 s pulse repetition delay). In each case, the cross-polarization contact time was 1 ms

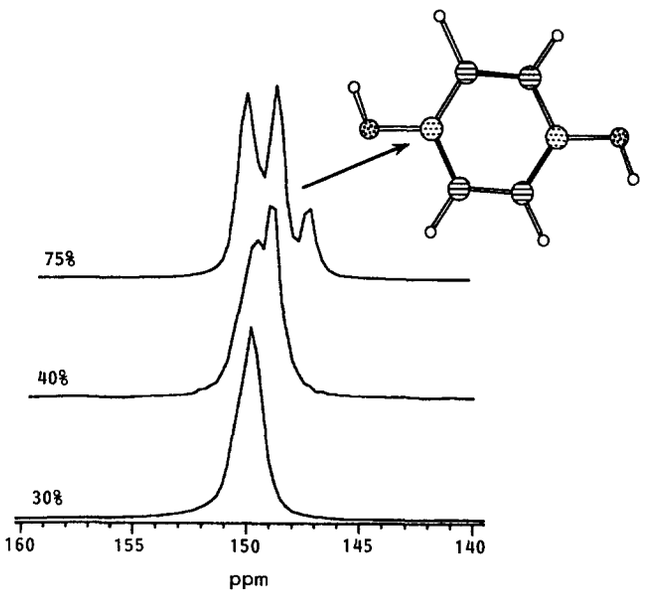

Figure 4 High-resolution solid state n.m.r. signals of the two phenolic carbons of hydroquinone in methanol-cast blends with PEO. The mole per cent of hydroquinone is indicated on the left of each spectrum. In each case, the cross-polarization contact time was 1 ms and the pulse sequence repetition delay was 2 s

represent the α-form, and a distorted modification of the α-form due to the presence of PEO, because the β- and γ-modifications transform spontaneously to the α-form[26]. Crystal symmetry arguments suggest that six ^{13}C n.m.r. signals should represent the four protonated aromatic carbons, if three crystallographically inequivalent resonances are observed for the two phenolic carbons. Most likely, two of the protonated aromatic carbon signals overlap and, hence, only five resonances are detected on the right side of *Figure 3A*. Chemical shift estimates[29] based on a wealth of tabulated data for monosubstituted benzene compounds in solution predict that the phenolic carbon signal should resonate at 148.5 ppm and the protonated aromatic carbon resonance should appear at 116.1 ppm. Hence, the solution and solid state ^{13}C chemical shifts for hydroquinone are quite similar, except for the crystallographic splittings observed in the solid state. The narrow linewidths in *Figure 3A* suggest that much more long-range order persists in the pure crystal relative to the complex. It is rather obvious that the crystal structure of hydroquinone (α-form) is modified by PEO in the aqueous precipitate.

The data in *Figures 4* and *5* illustrate concentration dependence of hydroquinone's phenolic and protonated aromatic carbon signals, respectively, in methanol-cast blends with PEO. The lineshapes at 30 mol% hydroquinone in the lowermost spectra of *Figures 4* and *5* are similar to those of the aqueous precipitate. For the blend containing 75 mol% hydroquinone that was prepared from methanol solution, the resonances for both types of aromatic carbons in the uppermost spectra of *Figures 4* and *5* reveal chemical shift multiplicities that mimic those in undiluted hydroquinone (see *Figure 3A*). This indicates that the 75 mol% blend contains slightly disordered crystals of hydroquinone because the chemical shift multiplicity is preserved in the blended state, but

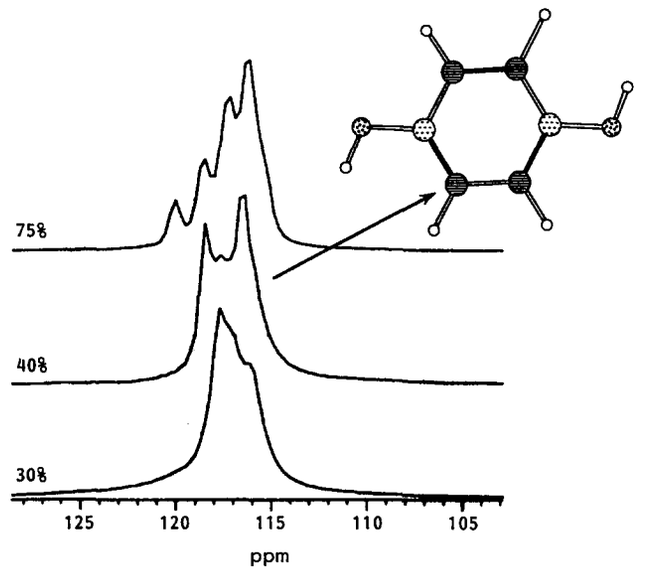

Figure 5 High-resolution solid state n.m.r. signals of the four protonated aromatic carbons of hydroquinone in methanol-cast blends with PEO. The mole per cent of hydroquinone is indicated on the left of each spectrum. In each case, the cross-polarization contact time was 1 ms and the pulse sequence repetition delay was 2 s

the resonances are broader relative to the undiluted crystal. Bieutectic phase behaviour is measured for methanol-cast blends of PEO and hydroquinone[31] via thermal analysis, as illustrated in *Figure 1*. An intermediate homogeneous solid solution (phase β) in the vicinity of 25–28 mol% of the small molecule separates two eutectic phase transformations at ~40 and ~80°C in the temperature–composition projection. Hence, the lowermost spectra in *Figures 4* and *5* at 30 mol% hydroquinone represent a mixture that is extremely close to the boundary of homogeneous phase β, exemplified by the aqueous precipitate in *Figure 3B*. At 75 mol% hydroquinone, chemical shift multiplicities for both types of aromatic carbon sites are observed

because the blend lies in the $\beta + \gamma$ two-phase region where one of the phases contains slightly disordered crystallites of hydroquinone.

Trieutectic mixtures of PEO with 2-methylresorcinol

With gentle stirring action, 2-methylresorcinol dissolves in distilled water to produce a colourful solution that is pink to light brown. The colour of the ternary aqueous mixture of PEO and 2-methylresorcinol progresses from light brown to dark brown, and the precipitate that forms is reddish brown. This precipitate dissolves in freshly distilled water but, unlike the previous case with hydroquinone, it does not redissolve in the supernatant. Solid state n.m.r. spectra in the methyl carbon chemical shift region for the undiluted small molecule and the aqueous precipitate of PEO with 2-methylresorcinol are illustrated in *Figure 6*. *Figure 6A* indicates that there are two n.m.r.-distinguishable methyl groups in the unit cell, possibly due to packing inequivalences. When 2-methylresorcinol forms a precipitate with PEO from aqueous solution, blending-induced interactions in this solid complex alter the lattice structure of 2-methylresorcinol and the molecules adopt a different crystallographic symmetry. This claim is based on the appearance of the methyl carbon resonance envelope illustrated in *Figure 6B*. Solid state n.m.r. spectroscopy identifies three crystallographically inequivalent methyl carbons in the precipitate, and two of these signals appear at the same chemical shifts as those in undiluted 2-methylresorcinol. Broader resonance signals are observed for the aqueous precipitate, suggesting that the lattice structure of 2-methylresorcinol is slightly disordered in the blend with PEO.

The data in *Figure 7* illustrate concentration dependence for the phenolic carbon signal of 2-methylresorcinol in methanol-cast blends with PEO. Predictions based on solution-state ^{13}C n.m.r. for monosubstituted benzene compounds suggest[29] that the phenolic carbon resonates at 159.0 ppm. Solid state data for the blends in *Figure 7* reveal three n.m.r.-distinguishable signals at 154.5, 156.0 and 157.0 ppm. Blend concentration spans a critical region of the temperature–composition phase diagram from 21 mol%

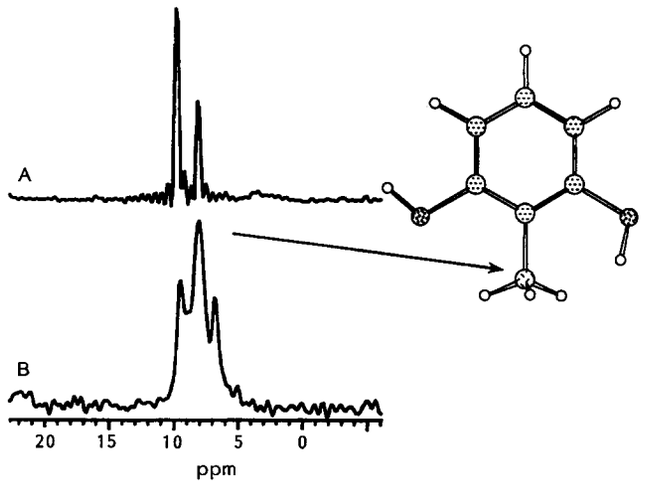

Figure 6 High-resolution ^{13}C solid state n.m.r. signals of the methyl group of 2-methylresorcinol in the undiluted crystalline state (A, 60 s pulse repetition delay) and in an aqueous precipitate with PEO (B, 2 s pulse repetition delay). In each case, the cross-polarization contact time was 1 ms

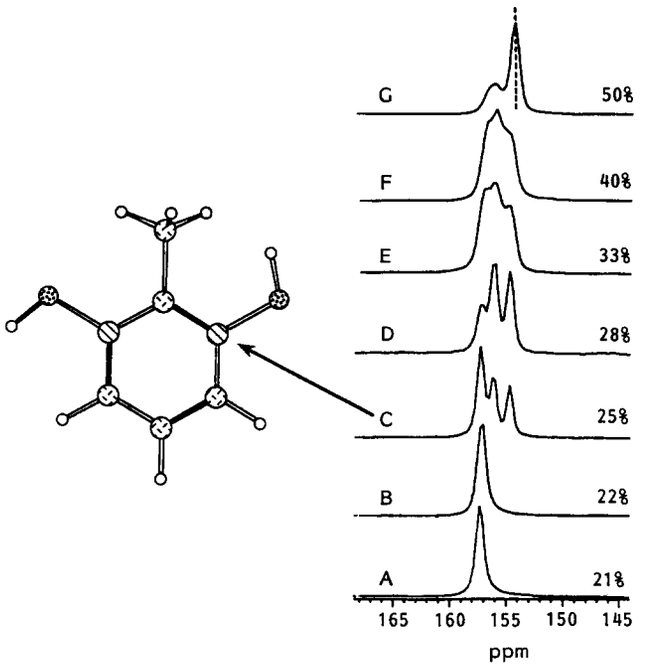

Figure 7 High-resolution solid state n.m.r. signals of the phenolic carbons of 2-methylresorcinol in methanol-cast blends with PEO. The mole per cent of 2-methylresorcinol is indicated on the right of each sectrum. The broken line in spectrum G identifies the phenolic carbon chemical shift of undiluted 2-methylresorcinol. In each case, the cross-polarization contact time was 1 ms and the pulse sequence repetition delay was 2 s

of the small molecule in spectrum A to 50 mol% in spectrum G. Two ambient-temperature molecular complexes at ~18–23 and ~35–45 mol% 2-methylresorcinol separate three eutectic phase transformations for this binary polymer/small molecule system as illustrated in *Figure 2*. Spectra A and B in *Figure 7* identify a single phenolic carbon chemical shift for the small molecule in homogeneous phase β that is 2.5 ppm downfield from the phenolic carbon signal in undiluted 2-methylresorcinol (on the pure-component boundary of phase δ). The spectrum of undiluted 2-methylresorcinol exhibits only one signal for the phase-sensitive phenolic carbon resonance at 154.5 ppm, and this chemical shift position is indicated by the broken line in spectrum G. At most, three phenolic carbon signals can be resolved in the overall resonance envelope when the blends contain 25 and 28 mol% 2-methylresorcinol (*Figures 7C* and *7D*). These three resonances are also observed with much less resolution in spectra E and F for blends that contain 33 and 40 mol% 2-methylresorcinol, respectively. Only two phenolic carbon n.m.r. signals are detected for a 50/50 mixture of the two components as illustrated in spectrum G of *Figure 7*. Correlations between the n.m.r. spectra in *Figure 7* and phase coexistence based on the temperature–composition projection in *Figure 2* are not straightforward, particularly over the concentration range that includes 25–40 mol% of the small molecule. Spectra A (21 mol%) and B (22 mol%) are consistent with one-phase (β) behaviour, and spectrum G at 50 mol% 2-methylresorcinol is consistent with macroscopic phase behaviour that reveals the coexistence of two phases (γ and δ).

The n.m.r. data in *Figure 8* illustrate the concentration dependence and spectroscopically detectable trieutectic response of the protonated carbon of 2-methylresorcinol

in the five-position of the aromatic ring, in methanol-cast blends with PEO. Predictions from a wealth of ^{13}C solution-state n.m.r. data suggest[29] that this carbon resonates at 127.3 ppm. Solid state data for the blends reveal that the C5 carbon in 2-methylresorcinol resonates at 124.5, 127.0 and 128.5 ppm. The latter of these three resonances is identical with the singlet at 128.5 ppm in the undiluted small molecule. Even though this aromatic carbon seems to be rather far removed from the interaction sites, hydrogen bonds between the hydroxyl protons in the small molecule and the ether oxygen in PEO (i) distort electron density in the π-orbitals of the ring, (ii) modify the crystal symmetry of 2-methylresorcinol in the blends, and (iii) affect the chemical shift of this distant site. The spectra in *Figure 8* suggest that two-phase coexistence is characteristic of both blends at $\sim 15°C$. For the 50 mol% mixture in the $\gamma + \delta$ two-phase region, one of the coexisting phases contains slightly disordered crystals of 2-methylresorcinol in phase δ that are n.m.r.-indistinguishable from the undiluted small molecule. This claim is supported by the phase diagram in *Figure 2* and based on the fact that the C5 aromatic signals resonate at 127.0 and 128.5 ppm in the upper spectrum of *Figure 8*. The chemical shift of this latter signal is identical to the singlet for undiluted 2-methylresorcinol on the pure-component boundary of phase δ. When the concentration of 2-methylresorcinol is reduced to 25 mol%, (i) two-phase ($\beta + \gamma$) behaviour at $\sim 15°C$ is suggested by the phase diagram in *Figure 2* and supported by ^{13}C n.m.r. in the lower spectrum of *Figure 8*, (ii) neither phase is crystallographically similar to undiluted 2-methylresorcinol because the signal at 128.5 ppm is absent, (iii) coexisting phase γ that produces a C5 aromatic carbon resonance at 127.0 ppm contains crystals that are extremely similar to those in the γ-phase of the 50/50 blend, and (iv) the new signal at 124.5 ppm represents a third type of n.m.r.-distinguishable crystal structure for 2-methylresorcinol in phase β that does not exist in the 50/50 blend. These observations are consistent with trieutectic response for this binary system

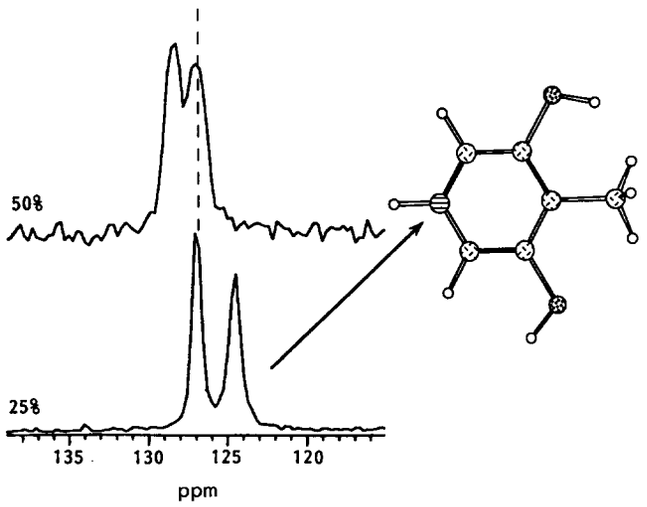

Figure 8 High-resolution solid state n.m.r. signals of the protonated carbon of 2-methylresorcinol in the five-position of the aromatic ring in methanol-cast blends with PEO. The mole per cent of 2-methylresorcinol is indicated on the left of each spectrum. The cross-polarization contact time was 1 ms and the pulse repetition delay was 2 s

Table 1 ^{13}C chemical shifts of the protonated carbon of 2-methylresorcinol in the five-position of the aromatic ring in blends with PEO that exhibit trieutectic phase behaviour

2-Methylresorcinol (mol%)	124.5 ppm (phase β)	127.0 ppm (phase γ)	128.5 ppm (phase δ)
Aqueous precipitate	√		
18	√		
21	√		
22.5	√		
25	√	√	
28	√	√	
30	√	√	
32.5	√	√	
35		√	
40		√	
50		√	√
55		√	√
70		√	√
Undiluted crystal			√

as illustrated in *Figure 2*. The molecular complex at ~ 18–23 mol% 2-methylresorcinol is designated phase β and the symmetry of the crystal lattice produces a C5 aromatic carbon resonance at 124.5 ppm. The homogeneous solid solution in the vicinity of 35–45 mol% 2-methylresorcinol is designated phase γ and its crystal symmetry generates a C5 aromatic carbon resonance at 127.0 ppm. Finally, the 2-methylresorcinol-rich region of the phase diagram that grasps the pure-component axis of the small molecule is phase δ and its crystal symmetry is consistent with a C5 aromatic carbon resonance at 128.5 ppm. Chemical shifts of the protonated carbon of 2-methylresorcinol in the five-position of the aromatic ring are summarized in *Table 1* for the undiluted crystal, the aqueous precipitate, and 12 methanol-cast blends. Solid state ^{13}C n.m.r. spectroscopy detects crystals that are characteristic of phase β exclusively in blends that contain 18–22.5 mol% 2-methylresorcinol. This concentration range identifies the intermediate homogeneous solid solution, designated phase β, that separates two eutectic transformations at 50 and 76°C. The aqueous precipitate contains 2-methylresorcinol with the same crystal symmetry as phase β, based on n.m.r. chemical shift data for the protonated carbon in the five-position of the aromatic ring (*Table 1*). Small molecule crystals that have the symmetries of phases β and γ are detected simultaneously for blends containing 25–32.5 mol% 2-methylresorcinol. This concentration range identifies the ($\beta + \gamma$) two-phase region in *Figure 2*. The crystal symmetry of 2-methylresorcinol in phase γ is detected exclusively for blends that contain 35 and 40 mol% of the small molecule. This is the second molecular complex that separates two eutectic transitions at 76 and 84°C. Two-phase behaviour is detected over the concentration range 50–70 mol% 2-methylresorcinol where the ^{13}C n.m.r. chemical shifts characteristic of phases γ and δ are observed simultaneously. The crystal symmetry of undiluted 2-methylresorcinol is identified as phase δ. Phase α represents a PEO-rich region that hugs the pure-component axis of the macromolecule. To date, phase α has not been observed via ^{13}C n.m.r. of the C5 aromatic carbon in 2-methylresorcinol for blends necessarily containing $< \sim 18$ mol% of the small molecule because of (i) the low concentration of

2-methylresorcinol in phase α, and (ii) signal-to-noise restrictions. The data in *Table 1*, *Figure 2* and *Figure 8* provide convincing evidence that solid state ^{13}C n.m.r. spectroscopy detects phase coexistence and molecular complexes for trieutectic blends of PEO with 2-methylresorcinol.

Effect of methyl group placement via mixtures of PEO with 5-methylresorcinol

A light brown solution is obtained when 5-methylresorcinol dissolves in distilled water. The ternary aqueous mixture of PEO with the small molecule is also brown but cloudy, and the precipitate that forms is brown. Similar to observations for the PEO/2-methylresorcinol precipitate, this precipitate dissolves in freshly distilled water, but not in the supernatant. The ^{13}C n.m.r. spectra of undiluted 5-methylresorcinol and its precipitate with PEO are the focus of *Figures 9* and *10*. Unlike 2-methylresorcinol, a methyl carbon in the 5-position of the aromatic ring is not expected to sterically interfere with the formation of hydrogen bonds that are characteristic of these complexes[30]. However, the interactions between dissimilar molecules are strong enough to affect electron density within the π-orbitals of the ring. Consequently, the crystal lattice is modified and all aromatic carbon n.m.r. signals of 5-methylresorcinol are sensitive to the presence of PEO in the precipitate.

Solid state n.m.r. data are illustrated in *Figure 9* for the phenolic carbons and the methyl-bonded aromatic carbon of 5-methylresorcinol. In the undiluted small molecule, *Figure 9A* reveals chemical shifts of 156.5 and 143.3 ppm, respectively, for these signals, and predictions based on solution state n.m.r. of monosubstituted benzene compounds[29] give 158.5 and 139.3 ppm, respectively. *Figure 9B* reveals chemical shifts of 158.0 and 141.0 ppm for these same two ^{13}C n.m.r. signals. Hence, the phenolic carbon signal shifts 1.5 ppm downfield in the precipitate with PEO, and the methyl-bonded aromatic carbon signal shifts 2.3 ppm upfield. For a methanol-cast blend containing 70 mol% 5-methylresorcinol, one observes both phenolic carbon resonances at 156.5 and 158.0 ppm, suggesting that the 70 mol% mixture lies in a two-phase region of the phase diagram at the temperature of the n.m.r. experiment. The same conclusion is drawn by focusing on the methyl-bonded aromatic carbon of 5-methylresorcinol in the 70 mol% blend cast from methanol. The data are consistent with bieutectic phase behaviour for the PEO/5-methylresorcinol binary system. *Figure 9A* is characteristic of the small-molecule-rich phase that hugs the pure-component axis of 5-methylresorcinol, and *Figure 9B* identifies the critical component in the single intermediate homogeneous solid solution that separates two eutectic phase transitions.

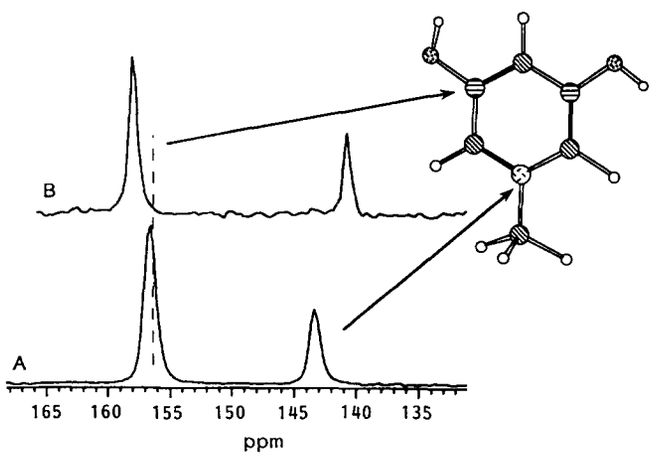

Figure 9 High-resolution ^{13}C solid state n.m.r. signals of 5-methylresorcinol in the undiluted crystalline state (A, 60 s pulse repetition delay, 10 Hz line broadening) and in an aqueous precipitate with PEO (B, 2 s pulse repetition delay, 5 Hz line broadening). In both cases, the cross-polarization contact time was 1 ms. The phenolic carbon resonance at 155–160 ppm is on the left side of the figure, and the methyl-bonded aromatic carbon resonance at 140–145 ppm appears on the right side of the figure

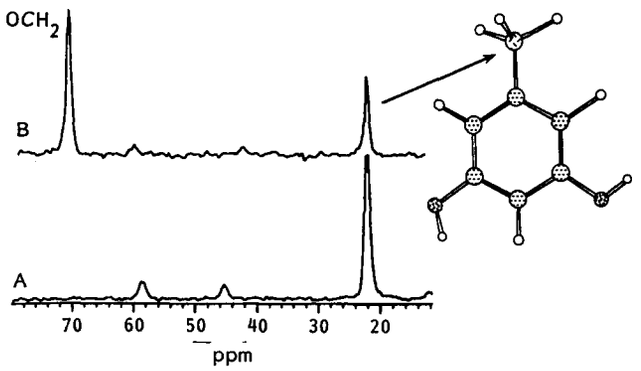

Figure 10 High-resolution ^{13}C solid state n.m.r. spectra of the methyl group in 5-methylresorcinol at 22 ppm on the right side of the figure. Spectrum A is representative of the undiluted crystalline state of the small molecule (60 s pulse repetition delay, 10 Hz line broadening), and spectrum B is derived from an aqueous precipitate with PEO (2 s pulse repetition delay, 5 Hz line broadening). In both cases, the cross-polarization contact time was 1 ms. The OCH_2 resonance of PEO at ~70 ppm appears in spectrum B on the left side of the figure. Two weak signals at 45 and 58 ppm in spectrum A represent spinning sidebands of the aromatic carbon centrebands of 5-methylresorcinol

The final comments in this paper focus on the methyl carbon signal of 5-methylresorcinol and the non-interacting nature of the methyl group in the aqueous precipitate with PEO. Solid state n.m.r. data in *Figure 10* reveal that the methyl carbon resonance at 22.0 ppm is not affected by the blending process. In contrast, the methyl carbon in 2-methylresorcinol is responsible for trieutectic phase behaviour in blends with PEO, and its n.m.r. signals illustrated in *Figure 6* indicate that the symmetry of 2-methylresorcinol is reduced in the crystal lattice of the precipitate relative to undiluted 2-methylresorcinol. The data in *Figure 9* reveal that PEO/5-methylresorcinol interactions in the aqueous precipitate (i) distort electron density in the π-orbitals of the ring, and (ii) alter the crystal lattice structure of 5-methylresorcinol as detected by the n.m.r. signals of the phenolic and C5 aromatic carbons. However, the n.m.r. data in *Figure 10* suggest that electronic distortions in the π-orbitals of the ring due to hydrogen bond formation between dissimilar molecules are not strong enough to affect the solid state n.m.r. chemical shift of the methyl carbon. Consequently, a methyl substituent in the five-position of the aromatic ring acts as an inert group in solid state complexes with PEO. The bieutectic phase behaviour of PEO and resorcinol is preserved when resorcinol is replaced by 5-methylresorcinol[1]. In contrast, three eutectic phase transformations dominate the temperature–composition projection of the phase diagram when resorcinol is replaced by 2-methylresorcinol.

CONCLUSIONS

There are very few binary polymeric mixtures that exhibit multiple eutectic transitions in the temperature–composition phase diagram, but several systems have been identified that contain a single eutectic response[7–14]. The results described here encompass three PEO/small molecule systems that exhibit two or three eutectic phase transformations. Solid state n.m.r. spectroscopy is enployed as a diagnostic probe of this unique phase behaviour at the molecular level where the principles of classical thermodynamics cannot be used to interpret site-specific interactions. In this respect, the ability to detect phase coexistence and dissimilar crystal structures with a high-resolution spectroscopic technique complements macroscopic results from thermal analysis and allows high-temperature phase boundaries to be extrapolated to ambient temperature and below. Most of the aromatic carbon signals of hydroquinone, 2-methylresorcinol and 5-methylresorcinol are sensitive to the presence of PEO in aqueous precipitates and methanol-cast blends. This is a consequence of hydrogen bonding between the ether oxygen in the polymeric chain and the hydroxyl protons in the small molecules which generates different crystal structures relative to the undiluted small molecules and distorts electron density in the π-orbitals of the aromatic ring. This phenomenon gives rise to aromatic carbon chemical shifts in the critical small molecule component that serve as a diagnostic probe of phase coexistence. The ^{13}C n.m.r. linewidths suggest that the lattice structures of the molecular complexes are slightly disordered relative to the undiluted resorcinol-like small molecules, but the spectrosocpic data are not indicative of completely amorphous blends. This latter claim is supported strongly by the temperature–composition phase diagrams which reveal that first-order melting processes are measured for each mixture. Solid state n.m.r. data for the methyl carbon in 5-methylresorcinol suggest that the methyl group is inert in blends with PEO. However, the methyl group in 2-methylresorcinol is responsible for a trieutectic response in methanol-cast blends with PEO. There are three n.m.r.-distinguishable C5 aromatic carbon signals of 2-methylresorcinol which support the concept of trieutectic phase behaviour, and the methyl carbon signal is not spectroscopically inert.

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REFERENCES

1 Cheng, C. and Belfiore, L. A. *Polymer News* 1990, **15**, 39
2 Belfiore, L. A., Lutz, T. J., Cheng, C. and Bronnimann, C. E. *J. Polym. Sci., Polym. Phys. Edn* 1990, **28**, 1261
3 Cheng, C. and Belfiore, L. A. *Polym. Prepr.* 1989, **30**, 325
4 Cheng, C. and Belfiore, L. A. 'Proceedings of the Industry–University Advanced Materials Conference' (Ed. F. W. Smith), Vol. 2, Colorado Advanced Materials Institute, Golden, 1989, p. 622
5 Belfiore, L. A., Qin, C. and Pires, A. T. N. *J. Polym. Sci., Polym. Phys. Edn.* in press
6 Qin, C., Pires, A. T. N. and Belfiore, L. A. *Polym. Commun.* 1990, **31**, 177
7 Smith, P. and Pennings, A. J. *J. Mater. Sci.* 1976, **11**, 1450
8 Smith, P. and Pennings, A. J. *Polymer* 1974, **15**, 413
9 Smith, P., Alberda van Ekenstein, G. O. R. and Pennings, A. J. *Br. Polym. J.* 1977, 258
10 Smith, P. and Pennings, A. J. *J. Polym. Sci., Polym. Phys. Edn.* 1977, **15**, 523
11 Smith, P., Koningsveld, R., Schouteten, C. J. H. and Pennings, A. J. *Br. Polym. J.* 1980, 215
12 Wittmann, J. C. and St. John Manley, R. *J. Polym. Sci., Polym. Phys. Edn.* 1977, **15**, 1089
13 Wittmann, J. C. and St. John Manley, R. *J. Polym. Sci., Polym. Phys. Edn.* 1977, **15**, 2277
14 Gryte, C. C., Berghmans, H. and Smets, G. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 1295
15 Adamson, A. W. 'A Textbook of Physical Chemistry', Academic Press, New York, 1973, p. 456
16 Marsh, J. S. 'Principles of Phase Diagrams', McGraw-Hill, New York, 1935, p. 87
17 Lin, P., Clash, C., Pearce, E. M., Kwei, T. K. and Aponte, M. A. *J. Polym. Sci., Polym. Phys. Edn.* 1988, **26**, 603
18 Gashgari, M. A. and Frank, C. W. *Macromolecules* 1988, **21**, 2782
19 Wind, R. A., Anthonio, F. E., Duijvestijn, M. J., Smidt, J., Trommel, J. and DeVette, G. M. C. *J. Magn. Reson.* 1983, **52**, 424
20 Stejskal, E. O. and Schaefer, J. *J. Magn. Reson.* 1975, **18**, 560
21 Earl, W. L. and VanderHart, D. L. *J. Magn. Reson.* 1982, **48**, 35
22 Etter, D. E., Tucker, P. A. and Wittenberg, L. J. 'Thermal Analysis' (Eds R. F. Schwenker and P. D. Garn), Vol. 2, Academic Press, New York, 1969, pp. 829–850
23 Gutt, W. and Majumdar, A. J. 'Differential Thermal Analysis' (Ed R. C. MacKenzie), Vol. 2, Academic Press, New York, 1972, Ch. 29
24 Maartmann-Moe, K. *Acta Cryst.* 1966, **21**, 979
25 Lindeman, S. V., Shklover, V. E. and Struchkov, Yu. T. *Cryst. Struct. Commun.* 1981, **10**, 1173
26 Wallwork, S. C. and Powell, H. M. *J. Chem. Soc., Perkin Trans.* 1980, **2**, 641
27 Caspari, W. A. *J. Chem. Soc.* 1926, 2944
28 Powell, H. M. *J. Chem. Soc.* 1948, 61
29 Ewing, D. F. *Organic Magn. Reson.* 1979, **12**, 499
30 Myasnikova, R. M., Titova, E. F. and Obolonkova, E. S. *Polymer* 1980, **21**, 403
31 Myasnikova, R. M. *Vysokomol. Soedin.* 1976, **A19**, 564
32 Point, J. J. and Damman, P. *Macromolecules* 1992, **25**, 1184