Isolation of zwitterionic intermediates in the spontaneous copolymerization of 2-methyl oxazoline and methyl maleate

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We have found that 2-methyl oxazoline and methyl maleate can be spontaneously copolymerized at room temperature without added initiators. The copolymerization was found to proceed through a zwitterionic mechanism. The zwitterionic intermediate has been isolated and characterized by elemental analysis, ^{1}H n.m.r., ^{13}C n.m.r., and CH, CH_2, CH_3 ^{13}C n.m.r. subspectra with the distortionless enhancement by polarization transfer (DEPT) technique, and i.r. spectroscopy. It was also found that the polymer structure derived from the polymerization of the zwitterionic salt was essentially identical to that of the material resulting from the direct polymerization of 2-methyl oxazoline and methyl maleate.

(Keywords: zwitterionic polymerization; 2-methyl oxazoline; methyl maleate)

Introduction

Some nucleophilic monomers such as oxazolines are known to copolymerize with various electrophilic monomers without the need for added initiators. Such a polymerization, referred to as zwitterionic polymerization[1], is reported to proceed via zwitterionic intermediates. For example, a monomer having a nucleophilic site (Mn) reacts with a monomer of electrophilic nature (Me) to produce zwitterions which are initiating species. In turn, the subsequent reactions of zwitterions produce oligomeric zwitterions to produce polymers.

$$\text{Mn} + \text{Me} \rightarrow +\text{Mn-Me-}$$

$$+\text{Mn-Me-} + +\text{Mn-Me-} \rightarrow +\text{Mn--MeMn--Me-}$$

$$+\text{Mn--MeMn--Me-} \rightarrow +\text{Mn--(MeMn)}_{n+1}\text{--Me-}$$

$$+\text{Mn----Me-} + +\text{Mn----Me-} \rightarrow +\text{Mn-----MeMn-----Me-}$$

Thus, 2-oxazolines were known to copolymerize with many cyclic compounds such as β-propiolactone[2], propane sultone[3] and succinic anhydride[4]. Either 1:1 or 2:1 alternating copolymers were postulated from such monomer pairs based on the above zwitterionic polymerization mechanism. The oxazoline monomers were also reported to copolymerize with various electron-deficient olefins such as acrylic acid[5], acrylamide[6], hydroxyalkyl acrylate[7] and ethylene sulphonamide[8]. In all of these studies, intermediate zwitterions have been claimed based on the structure of the final polymer. Although such zwitterions have frequently been postulated and sometimes proved with model compounds, there are no reports on the direct isolation of such an intermediate in the spontaneous copolymerization of oxazolines. The only related example of isolating a zwitterion intermediate was in the spontaneous copolymerization reaction between 2-phenyl-5,6-dihydro-4H-1,3-oxazine and acrylic acid[9]. However, the monomer involved was a very stable six-membered ring associated with the phenyl group, and the polymerization was not at all efficient. It had to be kept for 10 days at 5°C and subsequently heated at 100°C for 5 h to obtain only 25% polymer conversion. It is also known that these zwitterionic copolymerizations did not produce high molecular weight polymers, probably due to the difficulty involved in the increasing charge separation between the positive and negative ends of propagating chains.

Here we report a copolymer system with a reasonably high molecular weight which proceeds by a zwitterion polymerization mechanism via a potentially stable zwitterion intermediate. Also, we demonstrate that the zwitterionic intermediate plays an important role in the polymerization process by isolating such an intermediate, characterizing the material in detail and subsequently polymerizing the intermediate zwitterionic material.

Experimental

2-Methyl oxazoline (Aldrich Chemical Co.) was distilled, dried over magnesium sulphate, filtered and stored over molecular sieves (3 Å) prior to use. Methyl maleate was synthesized by reacting maleic anhydride with methyl alcohol without using solvents. *N*,*N*-dimethylformamide (DMF) was distilled at reduced pressure from barium oxide. The reagent grade acetone and diethyl ether were used as received.

All polymerization reactions were carried out in either sealed tubes or flame-dried glassware equipped with a tightly fitted rubber septum under a nitrogen atmosphere. For n.m.r. experiments, the polymerization was carried out in the n.m.r. tubes.

I.r. spectra were recorded with a Perkin Elmer 1420 ratio recording i.r. spectrophotometer. A Varian EM360 spectrometer was used to record the 60 MHz ^{1}H n.m.r. spectra. A General Electric GN 300 n.m.r. spectrometer was used to record the 300 MHz ^{1}H n.m.r. spectra. Natural abundance ^{13}C n.m.r. spectra were recorded on a General Electric GN 300 n.m.r. spectrometer operating at 75 MHz.

Elemental analyses were performed by Galbraith Laboratories (Knoxville, TN, USA).

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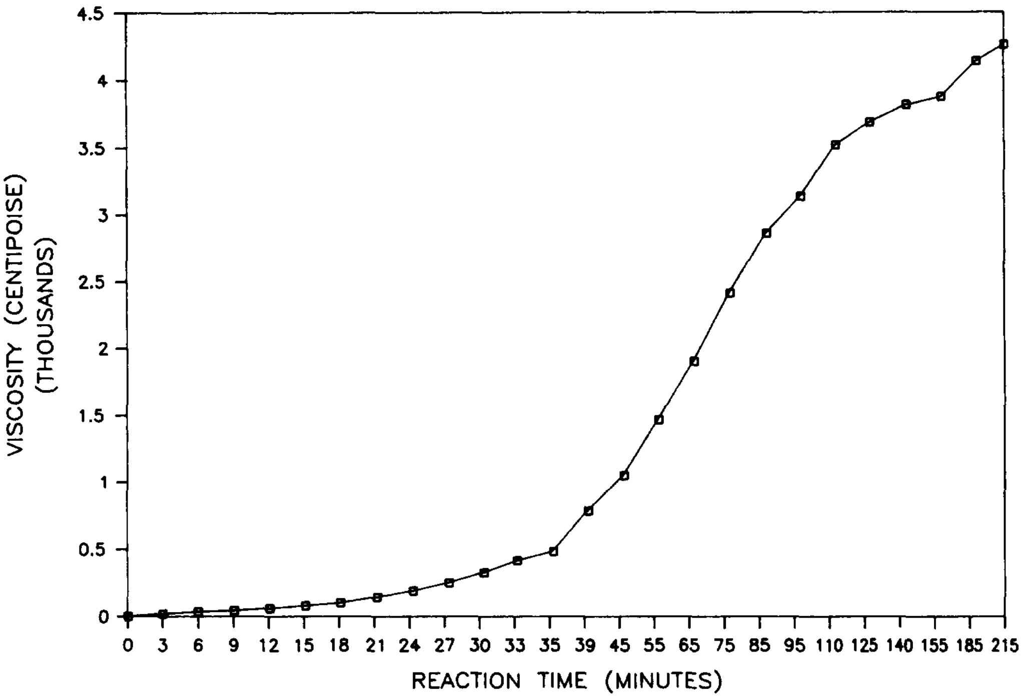


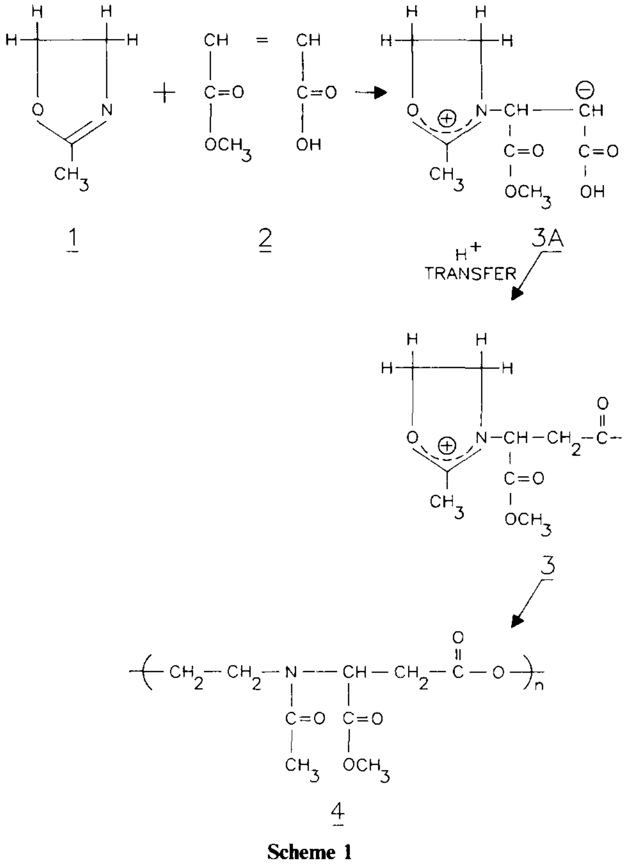
Figure 1 Effect of reaction time between 2-methyl oxazoline and methyl maleate on the Brookfield viscosity

For molecular weight measurements, a size exclusion chromatography (s.e.c.) system equipped with an LDC/Milton Roy model KMX-6 low angle laser light scattering (LALLS) detector was used. Size exclusion separation was provided by a Polymer Laboratories PL gel column set consisting of 10^5, 10^4, 10^3 and 10^2 Å columns. Molecular weights were obtained by using the LALLS outputs and a constant value for the specific refractive index increment (dn/dc).

A Brookfield digital viscometer model DV-I (Brookfield Engineering Laboratories, Inc.) was used to monitor the viscosity of the polymerizing solution. The Brookfield viscosity measures the torque resulting from the rotation of a spindle inside a sample chamber through which the sample flows continuously.

Results and discussion

We found that 2-methyl oxazoline can be spontaneously copolymerized with methyl maleate with the generation of highly exothermic heat at room temperature without initiators. For instance, upon mixing equal moles of methyl maleate and 2-methyl oxazoline, a dramatic increase in viscosity was noted, resulting in highly viscous polymeric materials. The Brookfield viscosity[10] was measured with reaction time. The relationship between viscosity and reaction time of 2-methyl oxazoline and methyl maleate is shown in *Figure 1*. After 140 min of reaction time, it was impossible to stir the reaction mixture. The reaction product was extensively purified by dissolving in DMF and then coagulating with cold diethyl ether. Drying of the material under high vacuum resulted in brown-coloured powdery polymeric materials with 95% conversion. The weight average molecular weight of the material was found to be 20000 and the polydispersity was 2.3 based on s.e.c. results. The ^1H n.m.r. spectrum of the resulting polymeric material exhibited 4.1 ppm ($C\underline{H}_2$), 1.9 ppm ($C\underline{H}_3$), 3.5 ppm (OCH_3) and 3.4 ppm ($\underline{C}\underline{H}$). The broadness of all these peaks implied polymeric rather than monomeric materials. The i.r. spectrum of the material showed the ester carbonyl group at 1730 cm^{-1}, the amide carbonyl stretching band at 1640 cm^{-1} and the C–O–C ether stretching band at 1050 cm^{-1}.



Scheme 1

Based on both n.m.r. and i.r. evidence, the polymer structure was deduced as *4* in *Scheme 1*. Also, the polymerization mechanism of 2-methyl oxazoline (*1*) and methyl maleate (*2*) is postulated as shown in *Scheme 1*. The nucleophilic nitrogen site of 2-methyl oxazoline can attack, via a Michael-type addition reaction[11], the electron-accepting double bond of the maleate to produce an oxazolinium carbanion salt *3A*. The subsequent hydrogen transfer from the hydroxyl group to the anionic site will produce zwitterionic species *3* having both oxazolinium cations and carboxylate anions. The nucleophilic attack of the anion on the oxazolinium ring will yield the macro-zwitterionic species. The repetitive propagation will generate the polymer which has a structure such as *4*.

During the course of our mechanistic investigation on the copolymerization of oxazolines and maleates in various solvents, we found that polymerization is strongly dependent upon the solvent employed. The rate of polymerization appeared to be fast and resulted in high yields in a very polar solvent such as DMF. But in less polar solvents, such as acetone or methyl ethyl ketone, the polymerization did not proceed. Instead, we found that our postulated zwitterion *3* could be isolated in quantitative yields. For example, an equimolar mixture of 2-methyl oxazoline and methyl maleate reacted under acetone refluxing conditions to produce copious amounts of white crystals. Subsequent filtering and drying in the vacuum oven afforded white crystals in quantitative yields. The white crystal had a melting point of 140–142°C. Upon melting, the solid slowly turned brown with an increase in viscosity. The white crystalline material was insoluble in all common organic solvents including acetone and methyl ethyl ketone, but it was soluble in water. The material could be stored for an indefinite period under a nitrogen atmosphere with remarkable stability.

The ^1H n.m.r. spectrum (60 MHz, D_2O solvent) of the material was in good agreement with the postulated structure, exhibiting a singlet at 2.1 ppm (3H, $N{-}CO{-}C\underline{H}_3$), a doublet at 3.05 ppm ($J = 5.8$ Hz, 2H, $CH{-}C\underline{H}_2{-}COO$), a triplet at 3.4 ppm ($J = 5.2$ Hz, 2H, $-C\underline{H}_2{-}N-$), a singlet at 3.7 ppm (3H, $-C\underline{H}_3$), a triplet at 4.0 ppm (1H, $J = 5.7$ Hz, $N{-}C\underline{H}{-}C{=}O$) and a triplet at 4.35 ppm (2H, $J = 5.2$ Hz, $O{-}C\underline{H}_2-$). The structural assignment of the n.m.r. spectrum is shown in *Figure 2*. The i.r. spectrum of the material further confirmed the salt *3* by clearly exhibiting the ester carbonyl peak at 1730 cm^{-1}, and the carboxylate anionic carbonyl (COO^-) at 1580 cm^{-1}. The ^{13}C n.m.r. spectrum of the salt also supported the proposed structure by showing $\underline{C}H_3{-}C$ at 18 ppm, $\underline{C}H_2{-}COO^-$ at 33 ppm, $-\underline{C}H_2{-}N^-$ at 44 ppm, $O\underline{C}H_3$ at 52 ppm, $N{-}\underline{C}H-$ at 56 ppm and $\underline{C}H_2{-}O$ at 58 ppm. The carbonyl carbon peaks were exhibited around 170 ppm. The detailed peak assignments of the ^{13}C n.m.r. spectrum are shown in *Figure 3*. Also *Figure 4* describes the distortionless enhancement by polarization transfer (DEPT) experiments[12] to generate methyl, methylene and methine carbon subspectra. The CH_3 subspectra showed as positive peaks at 18 ppm ($C{-}\underline{C}H_3$) and at

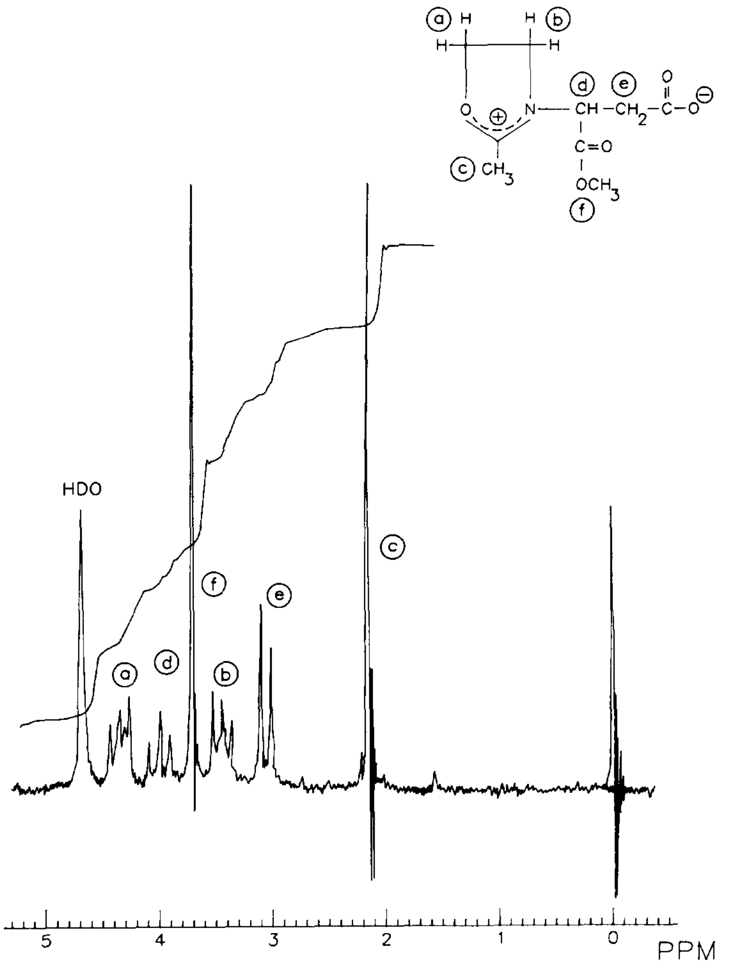


Figure 2 ^1H n.m.r. spectrum of the 2-methyl oxazoline/methyl maleate salt

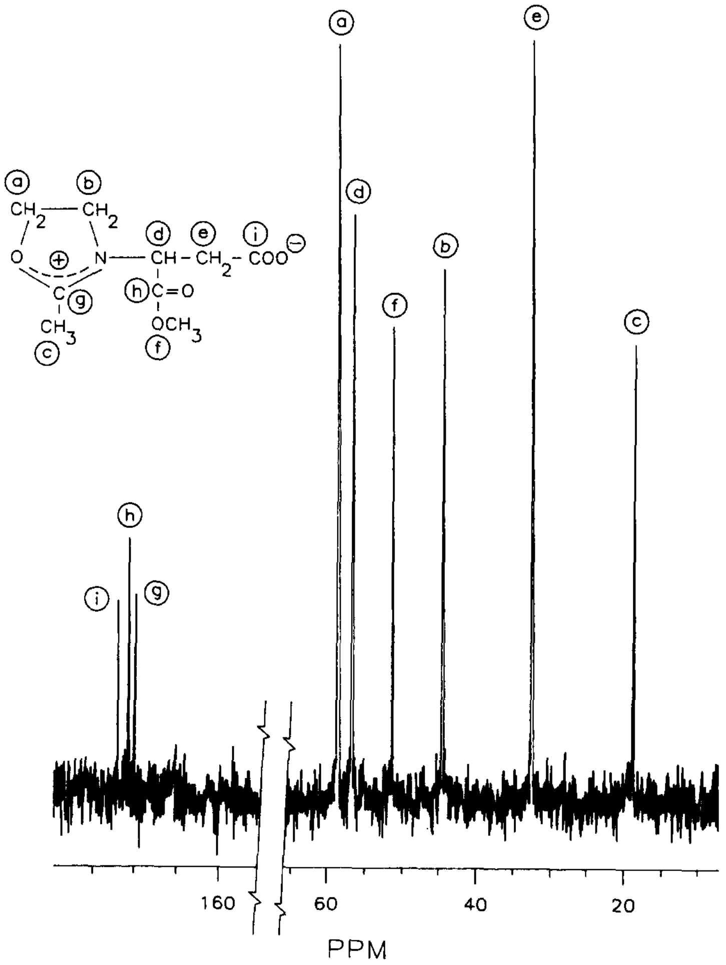


Figure 3 ^{13}C n.m.r. spectrum of the 2-methyl oxazoline/methyl maleate salt

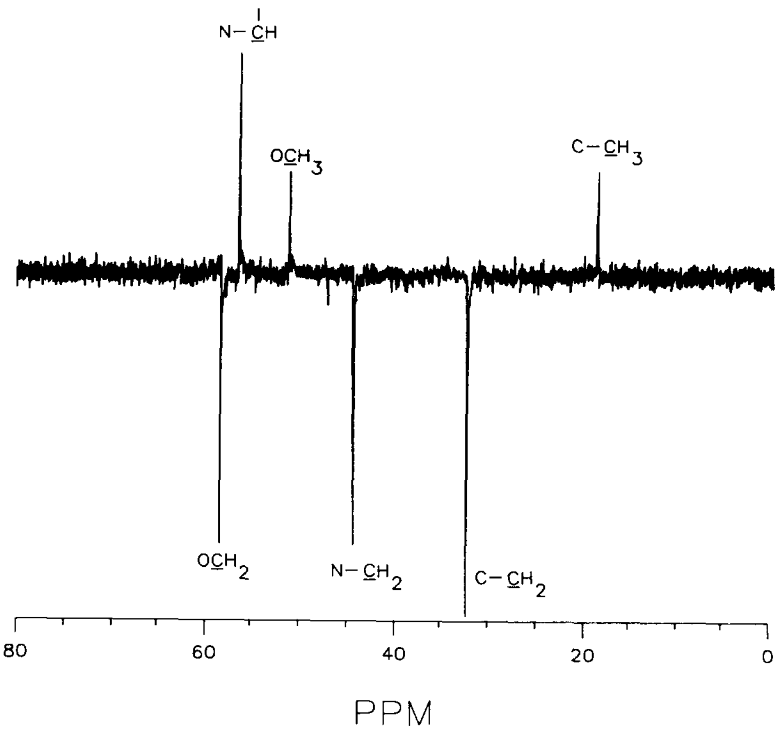
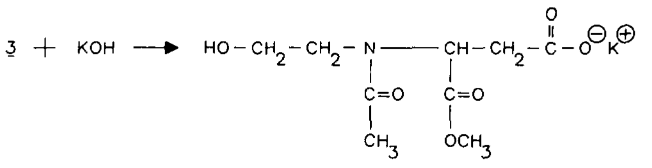


Figure 4 The DEPT subspectra of the 2-methyl oxazoline/methyl maleate salt



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Scheme 2

52 ppm ($O\underline{C}H_3$), and the CH subspectrum also showed a positive signal at 56 ppm ($N-\underline{C}H-$). Also, the three different CH_2 subspectra were exhibited as negative peaks at 33 ppm ($C-\underline{C}H_2$), 44 ppm ($N-\underline{C}H_2$) and 58 ppm ($O\underline{C}H_2$).

The elemental analysis data of the white crystal indicated that the salt indeed exists as the monohydrated form: calculated for $C_9H_{13}NO_5 \cdot H_2O$ salt: C, 46.35; H, 6.48; N, 6.00; found: C, 46.64; H, 6.54; N, 6.26.

In order to further prove the structure of the zwitterionic salt, the salt *3* was reacted with KOH. For example, 0.012 g of the salt and 0.005 g of KOH were dissolved in D_2O, and the n.m.r. spectrum of the reaction mixture exhibited a singlet at 3.45 ppm ($OC\underline{H}_3$), a singlet at 1.95 ppm ($C\underline{H}_3-C{=}O$), a multiplet at 2.95–2.15 ppm ($C\underline{H}_2-N$ and $C\underline{H}_2-C{=}O$), overlapped triplets at 3.55–3.85 ppm ($O-C\underline{H}_2$ and $C\underline{H}$). This indicated that the oxazolinium ring was cleaved by the strongly basic hydroxy ion as shown in *Scheme 2*.

The polymerization of the zwitterionic salt *3* was carried out as follows: for example, 0.404 g of the freshly prepared salt was vacuum sealed and then heated for 3 days at 140°C. The crystal slowly melted into a brown viscous liquid and the occurrence of polymerization was evident. The reaction mixture was dissolved in DMF and then coagulated into cold diethyl ether. The precipitate was collected by filtration under a nitrogen atmosphere. The polymer was so hygroscopic that it had to be handled under a nitrogen atmosphere. The i.r. and n.m.r. spectra of the resulting polymer derived from the salt are essentially identical to those of the directly polymerized product from 2-methyl oxazoline and methyl maleate without the isolation of the salt. The weight-average molecular weight of the polymer formed from the intermediate zwitterionic salt was found to be 30 000 with a polydispersity of 3.0 by s.e.c. It is interesting to note that the molecular weight of the salt-polymerized material is higher than that of the directly polymerized material. We are investigating the cause of this molecular weight difference.

In conclusion, we have shown that the zwitterionic intermediate plays an important role in the spontaneous copolymerization of 2-methyl oxazoline and methyl maleate. Detailed studies on the copolymerization of various substituted oxazoline and maleates are currently in progress and will be published elsewhere.

References

1 Kobayashi, S. and Saegusa, T. in 'Ring-Opening Polymerization Volume 2', Elsevier Applied Science, London, 1984
2 Saegusa, T., Ikeda, H. and Fujii, H. *Macromolecules* 1972, **4**, 354
3 Saegusa, T., Kobayashi, S. and Furukawa, J. *Macromolecules* 1977, **10**, 73
4 Kobayashi, S., Isobe, M. and Saegusa, T. *Macromolecules* 1982, **15**, 703
5 Saegusa, T., Kimura, Y., Ishikawa, N. and Kobayashi, S. *Macromolecules* 1976, **9**, 724
6 Saegusa, T., Kobayashi, S., Kimura, Y. and Ikeda, H. *J. Macromol. Sci. Chem.* 1975, **A9**(5), 641
7 Saegusa, T., Kimura, Y. and Kobayashi, S. *Macromolecules* 1977, **10**, 239
8 Saegusa, T., Kobayashi, S. and Furukawa, J. *Macromolecules* 1976, **9**, 728
9 Saegusa, T. and Kobayashi, S. *Macromolecules* 1977, **10**, 236
10 Dealy, J. M. 'Rheometers for Molten Plastics', Van Nostrand Reinhold, New York, 1982, p. 247
11 March, J. in 'Advanced Organic Chemistry', John Wiley, New York, 1985, p. 451
12 Doddrell, D. T., Pegg, D. T. and Bendall, M. R. *J. Magn. Reson.* 1982, **48**, 322