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Transesterification in polyethylene terephthalate–polyethylene naphthalene-2,6-dicarboxylate mixtures: a comparison of small-angle neutron scattering with NMR

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Abstract

Small-angle neuron scattering has been applied to mixtures of deuteropolyethylene terephthalate and polyethylene naphthalene-2,6-dicarboxylate that have been transesterified at temperatures of 543–573 K for a range of times. The change in scattering cross section has been analysed to provide values of the rate constants and, hence, the activation energies for the reaction. Excellent agreement for the rate constants is obtained with results reported by using NMR to analyse the reacted mixtures. Activation energies have been obtained as a function of the polyethylene terephthalate content of the mixtures and, additionally, for the transesterification in polyethylene naphthalene-2,6-dicarboxylate alone obtained from small-angle neutron scattering. The activation energy values range from 93 kJ mol^{-1} for pure polyethylene naphthalene-2,6-dicarboxylate to 160 kJ mol^{-1} for pure polyethylene terephthalate, with a distinct composition dependence being evident for polyethylene terephthalate weight fractions below 0.5.

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1. Introduction

The thermally induced random scission and recombination reaction in polyesters described as transesterification have been the focus of experimental investigation for some years now [1–15]. Where two chemically distinct polyesters are involved, spectroscopic methods can be used to great advantage to determine kinetic parameters. Mass spectrometry has also been used on the fragments obtained by chemical degradation of copolyesters formed by transesterification [8,16–19]. A polyester combination that has been much investigated is that of polyethylene terephthalate (PET) and polyethylene naphthalene-2,6-dicarboxylate (PEN). The preferred method to investigate the kinetics of the transesterification reaction between them is generally ^{1}H NMR because of the distinct differences in the spectra due to terephthalate and naphthoate sequences. In an earlier publication, we reported the extent of transesterification in PET and PEN, followed using NMR [20] and the role of the end groups and mechanism of transesterification in PET/PEN mixtures has also been clarified using NMR [21]. This method has also been used in a discussion of the reactive processing of PET and PEN [22].

Small-angle neutron scattering (SANS) has also been used to provide kinetic parameters of transesterification and is the only technique that can be applied to transesterification between chemically identical polyesters. One of the polyesters must be deuterated for this technique to be applied and we have used it to investigate transesterification in a number of polyesters [7,23,24] and to explore the influence of molecular weight and end groups on the reaction kinetics. The results support the conclusions from the NMR investigations, i.e. the predominant mechanism in transesterification is alcoholysis, the reaction can be significantly slowed by ‘end capping’ the hydroxyl ends and direct ester–ester interchange is almost negligible. There has been no direct comparison of the rate constants obtained by SANS with those obtained using NMR as yet. This aspect is addressed here, where we report a SANS investigation of the transesterification reaction between deutero PET and PEN over a range of temperatures and for a different composition of the polyester mixture. Additionally, we also present results of a SANS investigation of transesterification in PEN alone.

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2. Theory

In a mixture of hydrogenous and deuterated polyesters undergoing transesterification, the number of polymer molecules does not change, but the hydrogenous and deuterated repeat units become randomly distributed over all the molecules. Since the length of the isotopically identical sequences decrease and the molecules become more uniform in composition as transesterification proceeds, the intensity of neutron scattering decreases and it will appear that the molecular weight of the polymer molecules is decreasing. The correct interpretation of these observations was set out by Benoit et al. [25] and has been fully described by us in an earlier publication [24]. We do no more here than present the pertinent equations that are subsequently used in the analysis of our SANS data.

When the scattering cross section is plotted in the Zimm format, i.e. $(\mathrm{d}\Sigma/\mathrm{d}\Omega)^{-1}$ as a function of the square of the scattering vector, Q, the equation for the straight line is:

$$\frac{N_\mathrm{T}(b_\mathrm{H}-b_\mathrm{D})^2}{\mathrm{d}\Sigma/\mathrm{d}\Omega}=\frac{Q^2a^2}{12x(1-x)}+\frac{1}{2x(1-x)}\times\left[\frac{1}{x_\mathrm{D}}+\frac{1}{x_\mathrm{H}}-\frac{1}{x_\mathrm{Av}}+\frac{S(t)}{N_\mathrm{T}x(1-x)}\right] \tag{1}$$

where N_T is the total number of repeat units of all types in the reacting mixture, which has a mole fraction of D units of x. The number average degree of polymerisation of H and D polymers is x_H and x_D, respectively, and x_Av is the mole fraction weighted sum of these two degrees of polymerisation. The coherent scattering lengths of the H and D repeat units are b_H and b_D, respectively, and $S(t)$ is the number of efficient scissions that have taken place in time,

$$S(t)=N_\mathrm{T}x(1-x)\left[1-\exp\left(\frac{kN_\mathrm{T}t}{2}\right)\right] \tag{2}$$

with k being the second order rate constant of the transesterification reaction. The intercept at $Q=0$ when the scattering intensity is plotted according to Eq. (1) is:

$$z(t)=\frac{1}{2x(1-x)}\left[\frac{1}{x_\mathrm{D}}+\frac{1}{x_\mathrm{H}}-\frac{1}{x_\mathrm{Av}}+\frac{S(t)}{N_\mathrm{T}x(1-x)}\right] \tag{3}$$

When $t=0$, i.e. before any reaction, then $z(t)=z(0)$ and for subsequent times

$$z(t)=z(0)+\frac{1}{2x(1-x)}\left[\frac{S(t)}{N_\mathrm{T}(1-x)}\right] \tag{4}$$

Replacing for $S(t)$ from Eq. (2), then

$$z(t)=z(0)+\frac{1}{2x(1-x)}\left[-\exp\left(-\frac{kN_\mathrm{T}t}{2}\right)\right]$$

$$\therefore \ln[1-2x(1-x)(z(t)-z(0))]=-\frac{kN_\mathrm{T}}{2}t \tag{5}$$

A plot of the left-hand-side of Eq. (5) as a function of time should be linear with a negative slope from which the rate constant, k, can be calculated.

3. Experimental

3.1. Materials

Deutero polyesters

The procedure for the preparation of deuterated polyethylene terephthalate (DPET) has been described in an earlier publication and followed the method given by Gümther and Zachmann [26]. Deutero naphthalene-2,6-dicarboxylic acid and its polymer were prepared according to the methods published by Dorlitz and Zachmann [27]. Molecular weights of the polymers were obtained from intrinsic viscosity data in hexafluoro-2-propanol solutions and Mark–Houwink parameters for PET. The absence of such parameters for PEN means that the molecular weights for the PEN polymers are only approximate, but this was the procedure adopted in our earlier work on the use of NMR to obtain transesterification kinetics. The values for the PEN molecular weights from viscometry are not significantly in error based on the molecular weight obtained from the small-angle neutron scattering data for deuteroPEN in hydrogenous PEN mixtures before transesterification. These data gave a molecular weight of 15.8×10^3 g mol^{-1} for the molecular weight of the deuteropolymer.

3.2. Hydrogenous polyesters

PET and PEN were supplied by ICI and each separately dissolved in a phenol–trichlorobenzene mixed solvent (1:1) followed by precipitation into methanol and prolonged Soxhlet extraction with methanol of the precipitate. After drying under vacuum, the two polymers were recovered as powders and have been shown to be free of all traces of metallic catalyst residues [20]. The molecular weights of these polyesters and the deuterated versions are given in Table 1.

3.3. Small-angle neutron scattering

Samples for investigation by small-angle neutron scattering were prepared by co-dissolving the deuterated and hydrogenous polymers in the appropriate proportions in 1:1 phenol–trichlorobenzene and precipitation in methanol followed by Soxhlet extraction and drying. For

Table 1
Molecular weights of polyesters

Polymer	Molecular weight (10^3 g mol^{-1})
Hydrogenous PET	34.4
Hydrogenous PEN	27.3
Deutero PET	23.1
Deutero PEN	18.3

transesterification of DPEN/HPEN mixtures only one composition of mixture was used, a DPEN weight fraction of 0.5. For DPET/HPEN mixtures, DPET weight fractions of 0.25, 0.5 and 0.75 were used. Each mixture was compacted at room temperature by placing in an infrared die and applying a load of 5 tons under vacuum. The solid discs obtained were placed in a hole in a nickel plate, top and bottom covered with polyimide film and the whole assembly inserted between the platens of a previously heated laboratory press that were brought into contact with the nickel plate. A continuous flow of dry nitrogen suffused the region of the platens while the specimens were in place. The lowest temperature used was 543 K and the highest reaction temperature was 573 K. After the desired time of transesterification, the plate, polyester and polyimide films were quickly removed and plunged into ice water. The partially transesterified polyester sample, which was transparent and, thus, amorphous, was removed and dried under vacuum at 313 K.

Small-angle neutron scattering (SANS) data were collected using the LOQ diffractometer at the UK pulsed neutron source, ISIS, at the Rutherford Appleton Laboratory. All data were corrected for variations in sample thickness and transmission and converted to absolute scattering cross section, $d\Sigma/d\Omega$, before subtracting the background scattering. This latter was obtained as the weight fraction weighted sum of the scattering from the pure hydrogenous and pure deuterated polymers. The accessible range of scattering vector, Q, was from 0.01 to 0.25 $Å^{-1}$, all SANS data were collected at ambient temperatures and collection times were 1–2 h depending on weight fraction of deutero polyester and the extent of transesterification.

4. Results and discussion

4.1. DPET/HPEN mixtures

Fig. 1 shows the scattering cross sections obtained for different times of transesterification at 543 and 573 K for mixtures of DPET with HPEN with a DPET weight fraction of 0.5. There are some differences between these two data sets. At the lower transesterification temperature, the decrease in scattering cross section is not uniform with

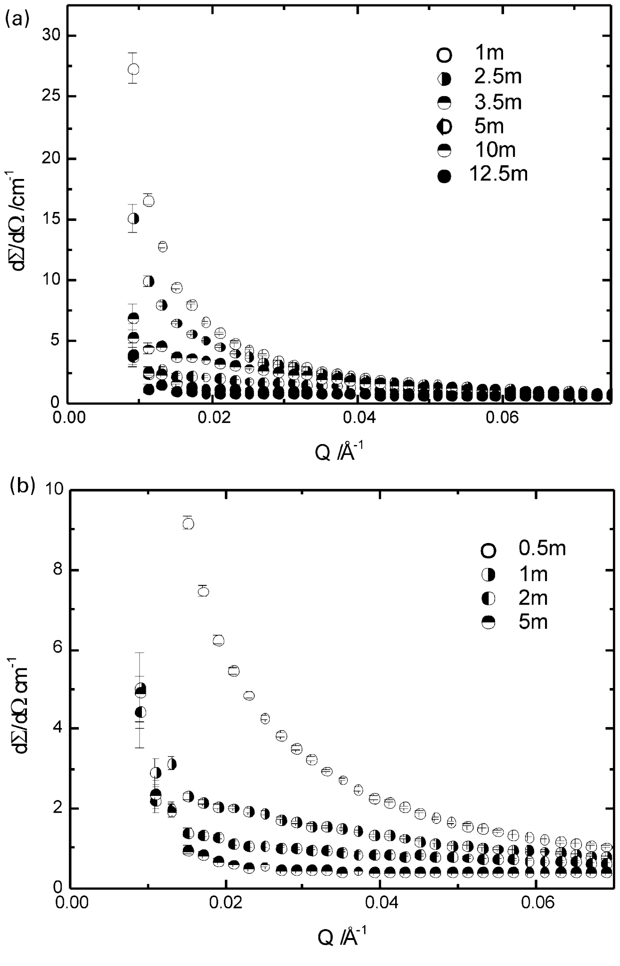

Fig. 1. Small-angle neutron scattering cross sections for DPEN/HPEN mixtures with a weight fraction of DPET of 0.5 as a function of transesterification time: (a) 543 K; (b) 573 K.

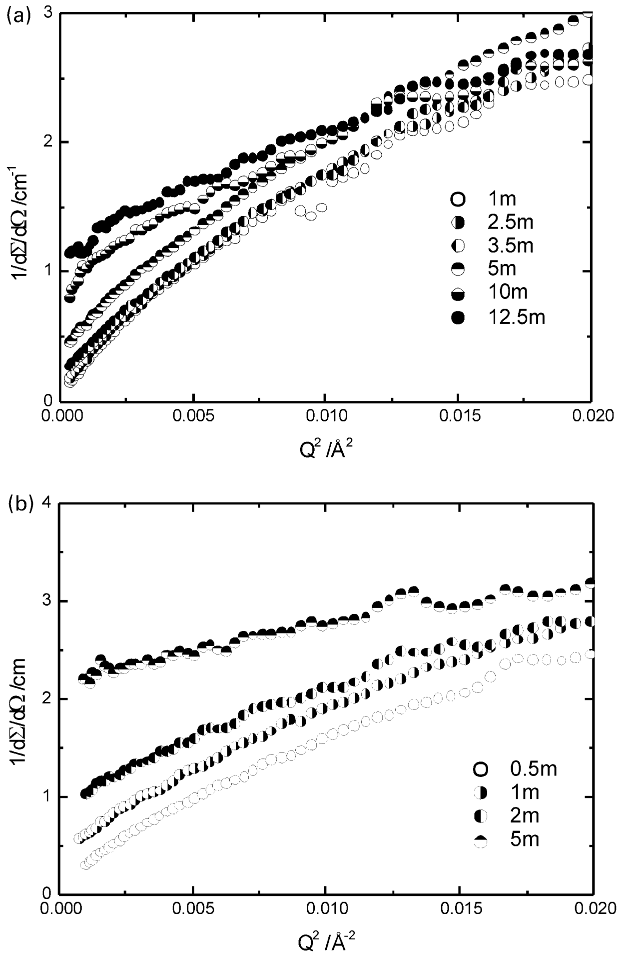

Fig. 2. Scattering cross section data for Fig. 1(a) and (b) plotted according to Eq. (1): (a) 543 K; (b) 573 K.

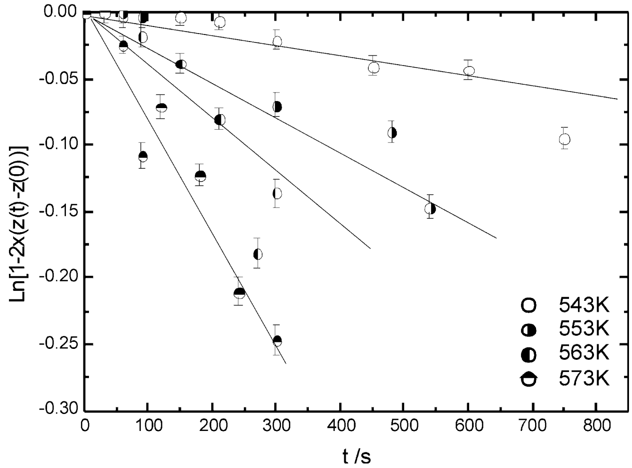

Fig. 3. Intercepts obtained from plots as in Fig. 2 plotted as for Eq. (5) for all temperatures of transesterification for the DPET/HPEN mixture with DPET weight fraction of 0.5.

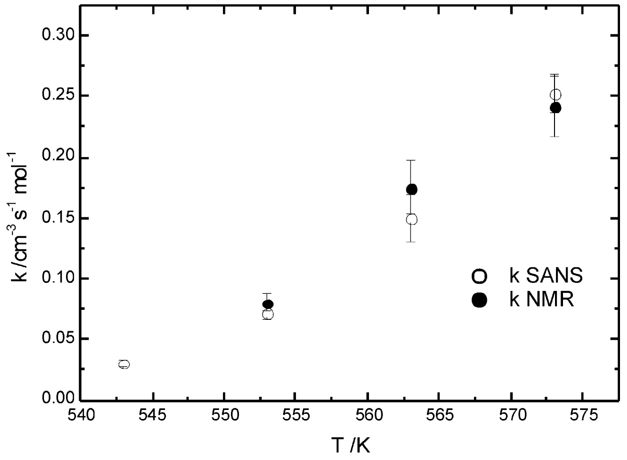

Fig. 4. Second order transesterification rate constants obtained by SANS and ^{1}H NMR (from Ref. [21]).

time, there being little difference in the scattered intensity between transesterification times of 1 and 2.5 min. After 3.5 min transesterification, there is a large decrease in the scattering cross section and for longer times the decrease in scattering cross section was more or less uniform with time. At the highest temperature used (Fig. 1b), the fall in scattering intensity with transesterification time is evident from the outset. This difference in behaviour is attributed to the initial immiscibility of PEN and PET. At 543 K, the PET is only just at the observed melting point and, until sufficient reaction has taken place to homogenise the blend completely, reaction will be confined to the regions where there is some intermixing. The reaction extends throughout the sample when sufficient PET/PEN copolymer is formed to homogenise the system. At 573 K, the two polyesters are sufficiently far above their respective melting points that thermal mixing promotes essentially uniform transesterification throughout the specimens and the scattering cross section falls uniformly with time from the outset. Scattering cross sections plotted according to Eq. (1) are shown in Fig. 2 and typical plots (i.e. using Eq. (5)) from which the rate constants were obtained are shown in Fig. 3 for transesterification temperatures of 543–573 K, evidently the reaction is considerably more rapid at 573 K. The somewhat scattered nature of these data notwithstanding, rate constants for the transesterification were obtained from the gradients of the least squares fits to the data plotted in Fig. 3. This procedure was also applied to DPET/HPEN mixtures where the weight fraction of DPET was 0.25 and 0.75, all the rate constants obtained for all mixtures and temperatures are given in Table 2.

Table 2
Second order rate constants for transesterification in DPET/HPEN mixtures

Temperature (K)	$w_{\mathrm{DPET}} = 0.25$ (k/10^{-2} cm^3 s^{-1} mol^{-1})	$w_{\mathrm{DPET}} = 0.5$ (k/10^{-2} cm^3 s^{-1} mol^{-1})	$w_{\mathrm{DPET}} = 0.75$ (k/10^{-2} cm^3 s^{-1} mol^{-1})
543	6.4 ± 0.4	3.0 ± 0.3	5.2 ± 0.8
553	12.3 ± 0.9	7.2 ± 0.6	9.0 ± 2
563	16.1 ± 1.8	15.0 ± 1.9	18.3 ± 3.3
573	–	25.2 ± 1.6	–

In an earlier publication, we reported rate constants for the transesterification in PET and PEN obtained by NMR analysis of specimens obtained for this same temperature range [21]. Fig. 4 compares the values of the rates constants obtained by SANS with those obtained by NMR analysis of mixtures with an initial weight fraction of PET of 0.5. Excellent agreement is obtained, suggesting that, although NMR observes changes in the local environment of protons on ethylene glycol residues and the SANS is determined by the changes of a long range nature, i.e. the average molecular weight of the polymer, both are governed by the same transesterification mechanism. Furthermore, we should note that NMR analysis becomes more accurate as reaction proceeds because the NMR signal associated with transesterification becomes stronger, whereas for the SANS the analysis is more difficult as reaction proceeds because

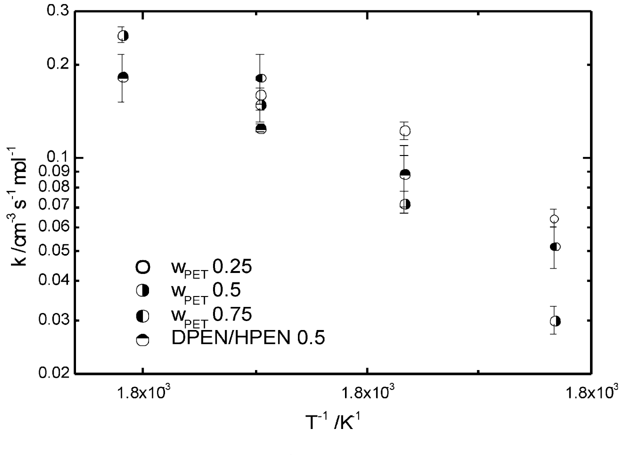

Fig. 5. Log$_{10}$(k) as a function of T^{-1} all obtained by SANS for DPET/HPEN mixtures and DPEN/HPEN mixture with a weight fraction of 0.5.

Table 3
Activation energies for transesterification in PET and PEN and their mixtures

Weight fraction	E_A (kJ mol^{-1})
PET	(SANS)
1	159 ± 30
0.75	158 ± 10
0.50	176 ± 2
0.25	127 ± 20
0	93 ± 9

Table 4
Second order rate constants for transesterification in DPEN/HPEN mixtures

Temperature (K)	k (10^{-2} cm^3 s^{-1} mol^{-1})
553	8.97 ± 1.2
563	12.5 ± 0.35
573	18.5 ± 3.2

the composition of the polyester molecules becomes more uniform. The contrast factor ($(b_H - b_D)^2$ in Eq. (1)) approaches zero and the scattering intensity decreases. Fig. 5 is an Arrhenius type plot of all the rate constants for the three compositions investigated and the activation energies obtained from linear least squares fits to these data are reported in Table 3.

4.2. DPEN/HPEN mixtures

The procedure outlined above was also applied to the mixture of DPEN and HPEN and the rate constants given in Table 4 were obtained for the three temperatures at which transesterification was investigated. The Arrhenius plot of these data is included in Fig. 5, the linear least squares fit giving an activation energy of 93 ± 9 kJ mol^{-1} (included in Table 3). We note that only four temperatures at most have been used to determine the rate constants and, moreover, the temperature range is not large, below 543 K the reaction is too slow and above 573 K the reaction is too rapid. Additionally for long reaction times at the highest temperature, additional reactions are evident leading to an apparent acceleration in the rate of transesterification.

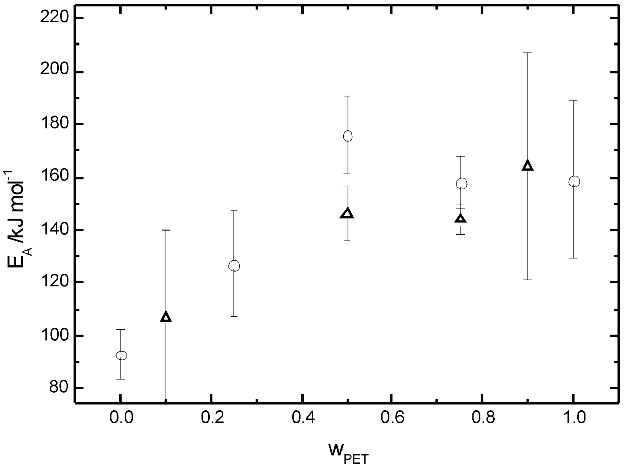

Fig. 6. Activation energies as a function of weight fraction of PET in PET/PEN mixtures. ○, SANS data; △, NMR data including previously unpublished values.

The activation energies in Table 3 have been plotted as a function of the composition of the polyester mixture in Fig. 6 and we have also included activation energies for PET/PEN mixtures obtained by NMR analysis of partially transesterified samples. Clearly, there is a composition dependence of the activation energy; lower values being associated with a higher content of PEN. Above a PET weight fraction of 0.5, the activation energy appears to have an asymptotic value of ca. 160 kJ mol^{-1}.

5. Conclusions

Small-angle neutron scattering has been applied to mixtures of deuteropolyethylene terephthalate and polyethylene naphthalene-2,6-dicarboxylate that have been partially transesterified. The rate constants obtained are in excellent agreement with those obtained by NMR analysis of solutions of the partially reacted mixtures, hence the same kinetic process is observed by the two different techniques. The kinetics of transesterification in PEN have been reported for the first time, a lower activation energy than for PET being obtained. A composition dependence of the activation energy is evident in the transesterification of PET with PEN.

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References

[1] Devaux J, Godard P, Mercier JP. Journal of Polymer Science—Polymer Physics Edition 1982;20:1901.
[2] Espinosa E, Fernandezberridi MJ, Maiza L, Valero M. Polymer 1993;34:382.
[3] Flory PJ. Principles of polymer chemistry. Ithaca, NY: Cornell University Press, 1952.
[4] Guo MM. Abstracts of Papers of the American Chemical Society 1996;211:230.
[5] Jacques B, Devaux J, Legras R, Nield E. Journal of Polymer Science Part A—Polymer Chemistry 1996;34:1189.
[6] Li MH, Brulet A, Keller P, Strazielle C, Cotton JP. Macromolecules 1993;26:119.
[7] MacDonald WA, McLenaghan ADW, McLean G, Richards RW, King SM. Macromolecules 1991;24:6164.
[8] Montaudo G, Puglisi C, Samperi F. Polymer Degradation and Stability 1991;31:291.
[9] Porter RS, Wang LH. Polymer 1992;33:2019.

[10] Wilkinson AN, Tattum SB, Ryan AJ. Polymer 1997;38:1923.

[11] Wilkinson AN, Cole D, Tattum SB. Polymer Bulletin 1995;35:751.

[12] Wong APY, Karim A, Han CC. Physica B 1996;221:301.

[13] Yamadera R, Murano M. Journal of Polymer Science A 1967;5:2259.

[14] Zheng WG, Wan ZH, Qi ZN, Wang FS. Polymer International 1994;34:301.

[15] Zheng WG, Qi ZN, Wang FS. Polymer International 1994;34:307.

[16] Montaudo MS. Macromolecules 1992;25:4264.

[17] Montaudo G, Montaudo MS, Scamporrino E, Vitalini D. Macromolecules 1992;25:5099.

[18] Montaudo G, Puglisi C, Samperi F. Journal of Polymer Science Part A—Polymer Chemistry 1993;31:13.

[19] Montaudo G, Puglisi C, Samperi F. Macromolecular Chemistry and Physics 1994;195:1241.

[20] Kenwright AM, Peace SK, Richards RK, Bunn A, MacDonald WA. Polymer 1999;40:5851.

[21] Collins S, Kenwright AM, Pawson C, Peace SK, Richards RW, MacDonald WA, Mills P. Macromolecules 2000;33:2974.

[22] Stewart ME, Cox AJ, Naylor DM. Polymer 1993;34:4060.

[23] Backson SCE, Richards RW, King SM. Polymer 1999;40:4205.

[24] Collins S, Peace SK, Richards RW, MacDonald WA, King SM. Macromolecules 2000;33:2981.

[25] Benoit HC, Fischer EW, Zachmann HG. Polymer 1989;30:379.

[26] Gümther B, Zachmann HG. Polymer 1983;24:1008.

[27] Dorlitz H, Zachmann HG. Journal of Macromolecular Science—Physics 1997;B36:205.