

Poly(ethylene terephthalate): a solid state condensation process

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A new method of solid state condensation of poly(ethylene terephthalate) is described. A low molecular weight pre-polymer with reactive end-groups is annealed at temperatures between 219° and 255°C. Samples with molecular weights from 3000 up to 16 000 are obtained. The materials as polymerized show very sharp melting peaks and high melting temperatures. The equilibrium melting point of PET was determined as $282^\circ \pm 2^\circ\text{C}$, the heat of melting as 26.1 ± 1.0 kJ/mol by suitable extrapolation of the data obtained from samples prepared by varying polymerization time and temperatures.

INTRODUCTION

Solid state condensation processes are often used to synthesize PET in order to reach high molecular weights and melting points^{1,2} as well as units of low diethyleneglycol content³.

Some years ago Miyagi and Wunderlich⁴ produced oligo (ethylene terephthalates) by etching folded chain PET crystals. The molecular weight of the resulting oligomers was found to be 2000 to 3000. By subsequent annealing of the oligomers below the melting point the molecular weight increased up to 20 000–30 000 due to transesterification reactions with simultaneous condensation at the crystal surfaces. We used a similar method but started from oligomers of very low degree of polymerization and with reactive end-groups. In this case, chain growth and crystal growth is due to end-group reaction as well as to transesterification.

EXPERIMENTAL

Purification of chemicals

Terephthaloyl chloride was refluxed for 12 h in dry n-heptane in the presence of thionyl chloride, recrystallized from n-heptane and dried *in vacuo*.

Bis(2-hydroxyethyl) terephthalate was synthesized and purified according to the method of Zahn⁵ (m.p. 107° – 108°C). Pyridine was refluxed over KOH and then distilled *in vacuo*. Tetrachloroethane (TCE) was refluxed for 25 h over CaH_2 and then distilled. CCl_4 and n-hexane (Merck) were used without further purification.

Precondensation

0.1 mol of bis(2-hydroxyethyl) terephthalate was dissolved in 200 ml TCE and 0.25 mol of pyridine. A solution of 0.1 mol of terephthaloyl chloride in 85 ml TCE was added dropwise. The reaction mixture was vigorously stirred for 48 h under a dry nitrogen atmosphere at room temperature. The precondensate precipitated during the reaction. It was washed several times with dry acetone and dried *in vacuo* at 50°C . The yield was about 70%.

Solid state condensation

0.2–2.0 g of the powdery precondensate were annealed in a test tube at a pressure below 1 mbar. The annealing temperature was controlled to within $\pm 0.5^\circ\text{C}$. At the beginning of the annealing process a vigorous evolution of HCl occurred, and a small amount of low molecular weight material was distilled out of the test tube. The total mass loss was about 10 to 15%. After annealing the polymer was quenched to room temperature.

Molecular weight determination

Intrinsic viscosities were determined in a 60/40 by wt mixture of phenol and TCE at 30°C in an Ostwald viscometer. The viscosity-average molecular weight was calculated according to Cha⁶.

Density measurements

Densities were determined in a density gradient column made up from mixtures of CCl_4 and n-hexane at 25°C . First, powder particles (diameter about 1 mm) were kept for 5 min in a mixture of both solvents (density 1.42 g/cm³) with ultrasonic cavitation in order to fill all voids in the sample by the solvents. Thereafter, the samples reached a stable position in the gradient column within a few hours. Untreated samples reached the same position only after two days.

D.s.c. measurements

All d.s.c. measurements were made with a Perkin–Elmer DSC–2 in unsealed aluminium pans in a dry nitrogen atmosphere with an empty aluminium pan as reference. Heating rates from 1.25° – $40^\circ\text{C}/\text{min}$ were selected. For melting temperature determination, sample weights from 0.3–1 mg were used. For the detection of the heat of melting, sample weights of 3–4 mg were chosen. Standards used for enthalpy and temperature calibration were indium (28.5 J/g, 156.6°C), tin (60.5 J/g, 231.9°C) and lead (23.0 J/g, 327.5°C). The experimental error was found to be $\pm 0.5^\circ\text{C}$ in temperature determination and about $\pm 3\%$ in the case of the heat of melting.

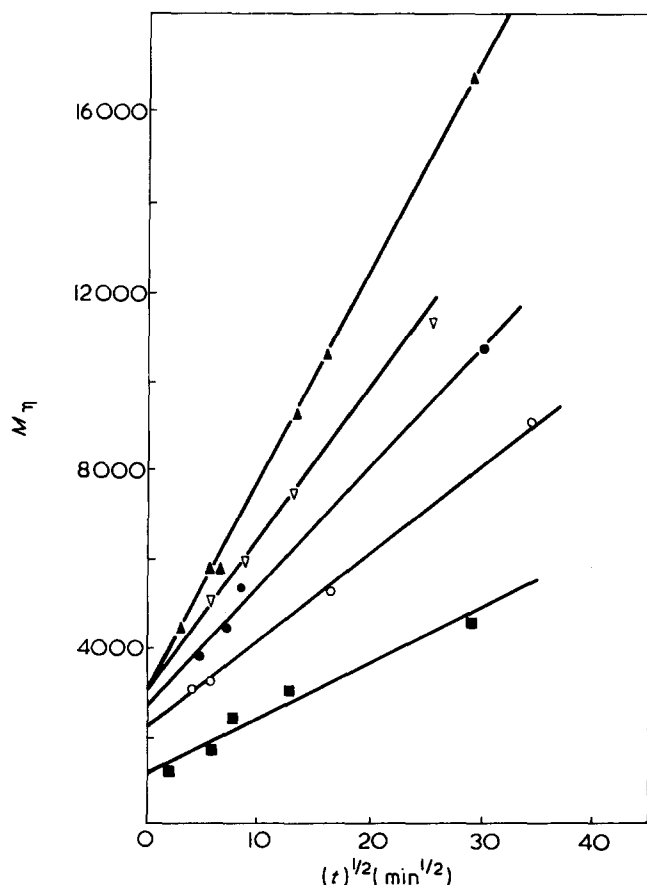
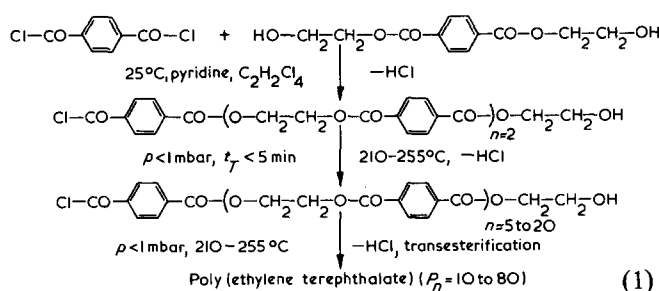


Figure 1 Viscosity-average molecular weight vs. the square root of the annealing time for solid state condensation of PET for different annealing temperatures: ▲, 254.2°C; ▽, 252.0°C; ●, 246.0°C; ○, 232.6°C; ■, 219.0°C

RESULTS AND DISCUSSION

Polycondensation process

The polycondensation process is described in equations (1).



(a) In the precondensation step terephthaloyl chloride is reacted in a tetrachloroethane solution in the presence of pyridine with an equimolar amount of bis(2-hydroxyethyl) terephthalate. The resulting low molecular weight precondensate is insoluble in the reaction mixture and precipitates. The content of chlorine is still about 5% by wt, from which an average degree of oligomerization of the order of 2 is calculated.

(b) At the beginning of the annealing process the precondensate powder is quickly heated up under vacuum to the annealing temperature t_T . Appropriate temperatures of annealing are of the order of 210° to 255°C. During the heating period, which should last about 3 to 5 min, a vigorous evolution of hydrogen chloride is observed. The

chlorine content drops below 2% and the degree of oligomerization increases up to a value between 5 and 20 depending on t_T . A certain amount of low molecular weight material, which is of the order of 10 to 15% distills out of the test tube.

It is important that the sample does not melt in the course of heating to the desired annealing temperature. The heating rate has to be selected such that the precondensate undergoes a sintering so that the melting point of the precondensate rises faster than the actual temperature of the sample.

(c) During the actual annealing period, the molecular weight increases by condensation of the still unreacted end-groups and transesterification takes place. Finally, porous powder of highly crystalline PET is obtained.

Increase of molecular weight

The viscosity-average molecular weight M_η was calculated from $[\eta]$ by Cha's equation⁶. Cha used an end-group method to establish his relationship. This method does not take into account that PET always contains cyclic oligomers⁷. Better methods of molecular weight determination are presently not available due to the poor solubility characteristics of PET. The only osmometric measurements thus far reported are on oligomeric copolyesters⁸.

The molecular weight of low molecular samples was cross-checked by end-group analysis. No significant differences between these values and those calculated according to Cha were noticed.

Figure 1 shows the increase of M_η with annealing time t_T . If M_η is plotted versus $(t_T)^{1/2}$ straight lines are obtained. The different lines represent different annealing temperatures. The slopes increase as do the intercepts of the lines with higher annealing temperature.

The linear dependence between M_η and $(t_T)^{1/2}$ does not hold for annealing periods longer than shown in the graph. This deviation is probably caused by the increasing influence of degradation reactions at very long annealing times.

Melting behaviour

Figure 2 shows a set of d.s.c. traces of samples annealed at 254°C for different times. The melting endotherms are

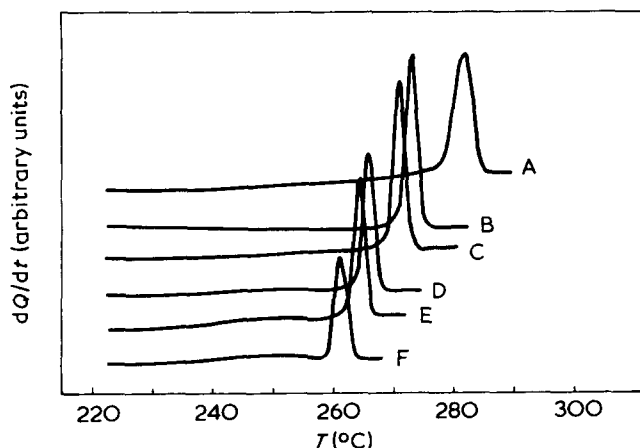


Figure 2 D.s.c. diagrams of solid state condensed PET for different times of annealing. Temperature of annealing 254°C, heating rate 10°C/min, sample weight 1 mg. A, 886 min; B, 260 min; C, 188 min; D, 46 min; E, 32 min; F, 10 min

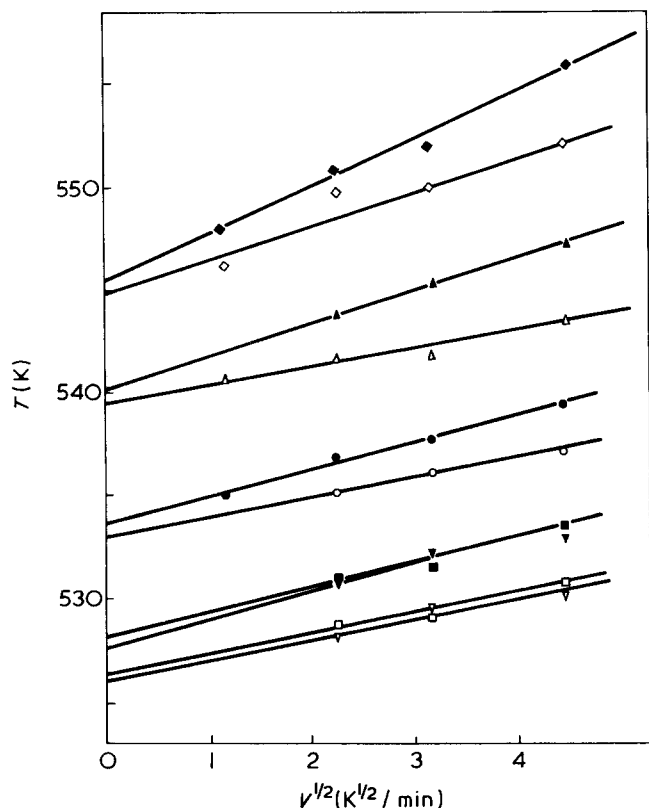


Figure 3 Shift of the melting peak position vs. square root of the heating rate for solid state condensed PET. $\diamond, \triangle, \square, \nabla$: extrapolated peak onsets. $\blacklozenge, \blacktriangle, \bullet, \blacksquare, \blacktriangledown$: peak maxima. Molecular weights: 16 800 (\diamond, \blacklozenge); 10 400 ($\triangle, \blacktriangle$); 7450 (\square, \bullet); 5100 (\square, \blacksquare), 4470 ($\nabla, \blacktriangledown$)

very sharp. The half-widths of these peaks are approximately 2° to 3°C at a heating rate of $10^\circ\text{C}/\text{min}$.

In the case of short annealing times, small premelting peaks are visible below the annealing temperature due to recrystallization effects. The recrystallization most likely arises during the quenching to room temperature, since during the heating in the d.s.c. experiment no crystallization peak was detected. Samples annealed for long times exhibit no premelting peaks.

Multiple peak behaviour with recrystallization effects was found for samples annealed at low temperature (e.g. 219°C).

It is known that overheating should be taken into account when discussing polymer melting and d.s.c. diagrams^{9,10}. Furthermore the slow response of the d.s.c. apparatus due to the slow heat transfer into the sample should be considered.

Because of the second effect, the position of the peak maximum as well as the extrapolated onset point of the peak depends linearly on the square root of the heating rate as shown in Figure 3. The peak maxima of oligomeric samples with molecular weights of about 4000 are shifted by 4°C at a heating rate of $20^\circ\text{C}/\text{min}$. The same shift is obtained in the case of metal standards used. With increasing molecular weight the peak maxima undergo shifts up to 9° or 10°C at the highest heating rate employed. This effect is clearly not only caused by the retardation of the d.s.c. apparatus but is also due to an overheating of the sample. Reports on very high melting temperatures (e.g. 290°C^2) of PET can thus be understood as artefacts.

In Figure 3 it is shown that the difference between peak

maximum and onset point at zero degree heating rate is only 1° to 2°C . The temperature of the peak maximum was defined as the melting point.

In Figure 4 the melting temperatures at zero heating rate are plotted for 4 different sample sets, each annealed at a certain temperature. For all t_T similar curves are found, but a remarkable shift to higher values is obtained for samples annealed at higher temperatures.

Similarly the heats of melting of the 4 sample sets were determined from the peak areas of the main melting peak and plotted vs. annealing time. The result is shown in Figure 5. The smallest values were found for those samples annealed at the highest temperatures. The samples annealed at 232°C exhibit only a slight linear dependence on the annealing time. The other samples clearly undergo a partial melting in the very beginning of the annealing process which results in a lower heat of melting of these samples than the precondensate (70 J/g). In Figure 5 the increase of the heat of melting following the initial partial melting is clearly expressed.

Properties of the pure crystalline phase of PET

For the pure crystalline phase of PET only few data are available. Extrapolation of the properties of semicrystalline samples to 100% crystalline material is difficult. PET

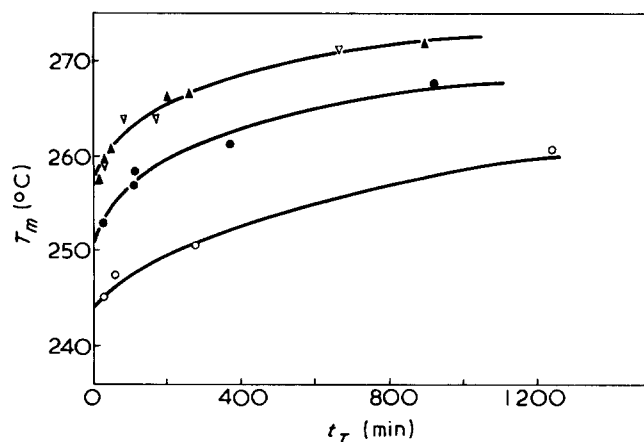


Figure 4 Melting temperature extrapolated to zero heating rate vs. the time of annealing for solid state condensed PET. Temperatures of annealing: \circ , 232.6°C ; \bullet , 246.0°C ; ∇ , 252.0°C ; \blacktriangle , 254.2°C

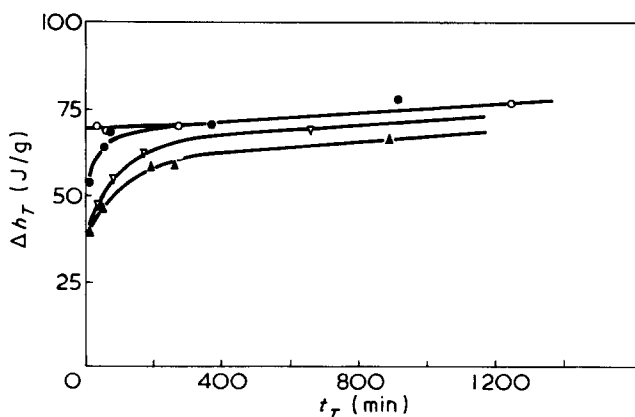


Figure 5 Heat of melting of solid state condensed PET vs. the time of annealing (without premelting peaks). For symbols see Figure 4

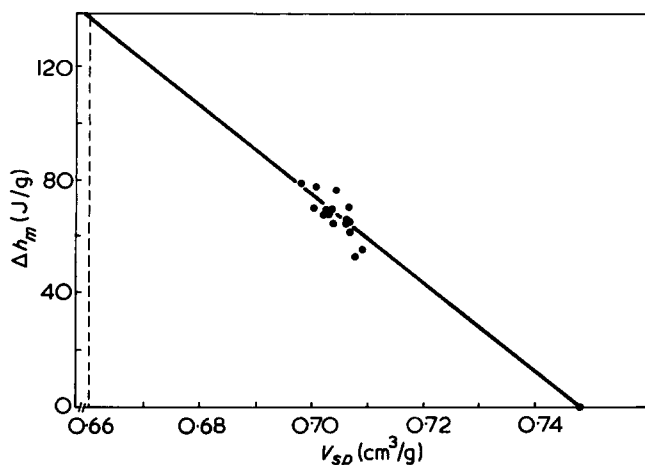


Figure 6 Heat of melting of solid state condensed PET vs. the specific volume: $v_{sp}^c = 0.660^{12}$; $v_{sp}^a = 0.748^{11,14}$

shows some influence of the thermal and mechanical history on the morphology of the amorphous phase. Müller¹¹ discussed the dependence of the density of the amorphous phase, ρ_a , on the degree of crystallization, but Fakirov¹² has since determined a new ρ_c which is 1.515 g/cm^3 , 4% higher than Bunn's value¹³ used by Müller. Therefore these calculations should be revised.

Lindner¹⁴ explained his X-ray results on drawn PET fibres with a third, intermediate phase having a density of about 1.357 g/cm^3 . As Stein has reported¹⁵, the superstructure of drawn amorphous material is influenced by the mechanical history. All these investigations were concerned with drawn samples, whereas our samples remain unstressed during annealing. Furthermore Illers¹⁶ found a linear dependence of the heat of melting on the specific volume for PET which had a high degree of crystallinity. At low degrees of crystallinity however the curve did bend and extrapolate to a value smaller than the normal specific volume of the amorphous phase $v_{sp}^a = 0.748 \text{ cm}^3/\text{g}^{11,14}$.

As our samples have crystallinities between 35 and 60% by wt they fall onto the linear part of the curve described by Illers. Therefore $v_{sp}^a = 0.748$ was used to extrapolate the heat of melting of the pure crystalline phase of PET.

We obtained $136 \pm 5 \text{ J/g}$ corresponding to 26.1 kJ/mol ($v_{sp}^c = 0.660 \text{ cm}^3/\text{g}^{12}$), as shown in Figure 6. In this graph the heat of melting, including the premelting peaks, was plotted versus the specific volume. Wunderlich⁴ found 105 J/g but using the wrong value of v_{sp}^c .

The equilibrium melting temperature T_m^0 was determined by Ikeda and Mitsuishi¹⁷ as 284°C from a plot following the procedure of Hoffmann and Weeks¹⁸. Using the data of Zahn¹⁹, Taylor²⁰ calculated the same value from the melting points of the dimer, trimer and tetramer ethylene terephthalate.

Recently, Hay²¹ published an expression, represented by equation (2) to determine the equilibrium melting point from oligomer melting points based on the Flory-Vrij theory²²:

$$T_m \approx T_m^0 \left[1 - \frac{T_m^0}{\Delta H_m^0} \cdot R/P_n \cdot \ln P_n(P_n - 1) \right] \quad (2)$$

Hay takes into account the entropy of mixing of the end-groups. Surprisingly, the theory which is valid for the melting of monodisperse extended oligomers seems also to hold for oligo(ethylene oxides)²¹.

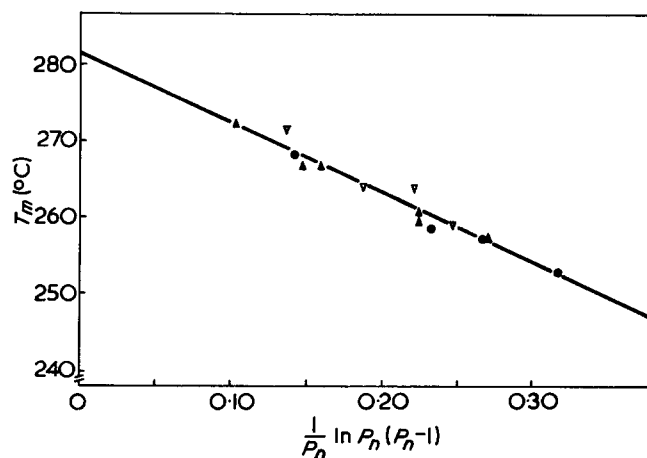


Figure 7 Melting point of solid state condensed PET vs. $1/P_n \cdot \ln [P_n(P_n - 1)]$. For symbols see Figure 4

As shown in Figure 7 the desired linearity of the melting point with $1/P_n \cdot \ln [P_n(P_n - 1)]$ is found even with different sets of samples, all annealed above 240°C . For this extrapolation P_n was approximately calculated from M_n . From the intercept, T_m^0 is $282 \pm 2^\circ\text{C}$ in good agreement with the literature. The heat of melting per mole of ethylene terephthalate unit, ΔH_m^0 , was calculated from the slope as 27.7 kJ/mol . This is only 5% higher than the value extrapolated in Figure 6.

It should be mentioned that Hay's assumptions are not fulfilled by the properties of the oligomers. Neither monodispersity nor very high crystallinity expected for extended chain oligomer crystals are found. Nevertheless, it is reasonable to assume that the oligomers form extended chains at high annealing temperatures considering the mechanism of chain growths and transesterification during sintering. X-ray small-angle scattering did not reveal any long spacings, probably because of the very strong void scattering due to the high porosity of the material. Morphological investigations are still in progress.

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REFERENCES

- 1 Jpn Kokai 76 73 592 (1974); Akimoto, I., Henmi, H., Shima, T. and Kusunose, T. *Chem. Abstr.* 1976, 85, 124 956
- 2 *Ger. Offen.* 2 415 729 (1974); Watase, H. and Shigetomi, K. *Chem. Abstr.* 1975, 82, 44 058
- 3 Penton, H. R. Jr and Bouman, H. *Polym. Prepr.* 1976, 17, 521
- 4 Miyagi, A. and Wunderlich, B. *J. Polym. Sci. (Polym. Phys. Edn)* 1972, 10, 2085
- 5 Zahn, H. and Krzikalla, R. *Makromol. Chem.* 1957, 23, 31
- 6 Cha, C. Y. *J. Polym. Sci. (Polym. Lett. Edn)* 1964, 2, 1069
- 7 Lüderwald, I., Urrutia, H., Herlinger, H. and Hirt, P. *Angew. Makromol. Chem.* 1976, 50, 163
- 8 Hashiboshi, M., Fukuda, T. and Kobayashi, S. *J. Macromol. Sci. (B)* 1969, 3, 525
- 9 Miyagi, A. and Wunderlich, B. *J. Polym. Sci. (Polym. Phys. Edn)* 1972, 10, 1401
- 10 Illers, K. H. *Eur. Polym. J.* 1974, 10, 911

- 11 Müller, E. H. *Colloid Polym. Sci.* 1974, **252**, 697
- 12 Fakirov, S., Fischer, E. W. and Schmidt, G. F. *Makromol. Chem.* 1975, **176**, 2459
- 13 Daubeney, R. de P., Bunn, C. W. and Brown, C. J. *Proc. Roy. Soc. (A)* 1954, **226**, 531
- 14 Lindner, W. L. *Polymer* 1973, **14**, 9
- 15 Misra, A., Stein, R. S., Chu, C., Wilkes, G. L. and Desai, A. B. *J. Polym. Sci. (Polym. Lett. Edn)* 1975, **13**, 303
- 16 Illers, K. H. 18th meeting 'Dechema-Arbeitsausschuss Polymerreaktionen' Frankfurt, 1977
- 17 Ikeda, M. and Mitsuishi, Y. *Chem. High Polym. Jpn* 1967, **24**, 378
- 18 Hoffmann, J. D. and Weeks, J. J. *J. Res. Nat. Bur. Stand. (A)* 1962, **66**, 13
- 19 Zahn, H. and Seidel, B. *Makromol. Chem.* 1959, **29**, 70
- 20 Taylor, G. W. *Polymer* 1962, **3**, 543
- 21 Hay, J. N. *Makromol. Chem.* 1976, **177**, 2559
- 22 Flory, P. J. and Vrij, A. *J. Am. Chem. Soc.* 1963, **85**, 3548