BUTTERWORTH HEINEMANN

Polymer Vol. 36 No. 22, pp. 4215–4222, 1995

0032-3861/95/$10.00+0.00

N.m.r. study of maleate (*cis*)–fumarate (*trans*) isomerism in unsaturated polyesters and related compounds

J. Grobelny
Institute of Polymer Chemistry, Polish Academy of Sciences, 41-800 Zabrze, Poland
(Received 27 February 1995; revised 18 May 1995)

Unsaturated polyesters and dicarboxy diesters from maleic anhydride and various diols were investigated by means of ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy. The carbons of diol units were found to be sensitive to maleate/fumarate transformation, enabling the process to be followed in detail. The *cis–trans* isomerism of dicarboxy diesters was described and related to the structure of the corresponding diols. The effects induced by the isomerism were examined separately for various carbons and, in the case of 1,2-propylene glycol, direct evidence was provided of the preference of CH over CH_2 groups in promoting the *trans* isomer. The results of the study on dicarboxy diesters along with data concerning the distribution of diol units along the chain were utilized to interpret the isomerism of unsaturated mixed polyesters.

(Keywords: unsaturated polyesters; *cis–trans* isomerism; nuclear magnetic resonance)

INTRODUCTION

The *cis–trans* isomerism taking place on polycondensation of maleic anhydride with diols has received much attention in the literature owing to the considerable practical consequences of this process. In fact, the presence of fumarate unsaturation sites plays a key role in determining the physical and chemical properties of the final crosslinked polyesters, owing to a higher reactivity of the *trans* isomer in copolymerization with vinyl monomers. Numerous works have been devoted to various aspects of the *cis–trans* interconversion[1–4]. The extent of the maleate–fumarate transformation was reported to depend on nature of the diols, presence of aromatic acids, concentration of catalyst, degree of polymerization as well as on the reaction temperature and time.

Early works employed polarographic and infra-red methods to study the isomerization reactions. The utility of high-resolution ^{1}H nuclear magnetic resonance spectroscopy (n.m.r.) in determining the maleate–fumarate ratio was demonstrated by Curtis *et al.*[2]. Unsaturated sites of the two types can also be distinguished by ^{13}C n.m.r.[3,5].

The most important structural parameters affecting the properties of unsaturated polyesters include the chemical composition, the degree of *cis–trans* isomerism and the extent of the double bond saturation via the addition of diol components. In our previous paper we proposed a method for structural characterization of unsaturated polyesters in terms of compositional sequence distribution[6]. The present work is focused on the problem of *cis–trans* isomerism in unsaturated polyesters and model dicarboxy diesters derived from maleic anhydride and various types of diol.

EXPERIMENTAL

Materials

Dicarboxy diesters were obtained by reacting various diols with excess amounts of maleic anhydride for 3 h at temperatures within the range of 60 to 205°C. Three types of diol were used in the syntheses carried out under a nitrogen atmosphere with no catalyst added: propylene glycol (PG), an oligomer of propylene oxide with $M_n \approx 550$ and $M_W/M_n = 1.2$ (PO) and 2,2-di(4-hydroxypropoxyphenyl)propane (propoxylated dian, PD).

Unsaturated polyesters derived from the same substrates were prepared by high-temperature (205°C) melt polycondensation.

The structures of PD and PO, as well as details concerning the preparation and composition of the polyesters, are given elsewhere[6].

Measurements

^{1}H and ^{13}C n.m.r. spectra were recorded at 20°C on a Varian VXR-300 multinuclear pulsed n.m.r. spectrometer operating at the ^{1}H resonance frequency of 300 MHz and the ^{13}C resonance frequency of 75 MHz. DEPT (distortionless enhancement by polarization transfer) experiments were used extensively throughout the study to confirm the assignments of the resonances. Chemical shifts were referenced to tetramethylsilane (TMS) serving as an internal standard.

The convolution difference resolution enhancement (CDRE) method was used to improve the spectral resolution and consequently the accuracy of integration and peak position determination. Convolution difference weighting is governed by a convolution difference time constant, *CD*, and a constant for convolution difference,

CCD. The CDRE function, $1 - CCD \times \exp(-t/CD)$, in addition to a decreasing exponential function, $\exp(-t/SE)$ (where SE stands for a sensitivity enhancement time constant), were applied to the FID (free induction decay) before the Fourier transformation[7–10]. The n.m.r. data processing with two weighting functions resulted in resolution enhancement and improvement in the sensitivity of the spectra.

RESULTS AND DISCUSSION

Dicarboxy diesters

The plots in *Figure 1* illustrate the progress in the *cis trans* isomerism *versus* temperature for the products obtained in the reactions of excess amounts of maleic anhydride with PG, PD and PO. As expected, respective dicarboxy diesters were found by ^{1}H n.m.r. to be the main products over the entire temperature range studied (60–205°C). The n.m.r. analysis revealed also the presence of small amounts of carboxy hydroxy monoesters at lower temperatures and longer dicarboxy esters above 140°C. The overall content of *trans* isomers was determined from ^{1}H n.m.r. spectra according to the method of Curtis *et al.*[2], using the areas of the signals due to fumarate ($\sim$6.9 ppm) and maleate ($\sim$6.4 ppm) olefinic protons. For PG-based esters the fumarate content was found to increase within the whole temperature range of study, attaining a value of $\sim$99% at 205°C. By contrast, for PD the isomerism was observed to start only above 150°C, while for PO above 120°C. At the end of the experiment the degrees of isomerism were found to be 95 and 82% for PD and PO, respectively.

During the past few decades, extensive studies on unsaturated polyester have clearly demonstrated that the structure of the diol exerts a profound influence on the degree of *cis–trans* isomerism. The transformation was attributed primarily to stereochemical effects and the resulting *trans* modification was concluded by examination of molecular models to be more stable energetically[1,2]. The higher energetic stability of the *trans* isomers may thus be considered as the driving force of the maleate → fumarate transformation. It was found that diols providing polyesters with denser structure (e.g. 1,2-propylene glycol, 2,2,4-trimethyl-1,3-pentanediol) tend to promote the highest degrees of isomerism. The lower accessibility of secondary hydroxyl groups or the considerable steric hindrance offered by such diols was concluded to account for the preference in reacting with *trans* isomer and consequently for the higher *cis–trans* conversion. On the contrary, lower degrees of isomerism were found for diols with widely separated hydroxyl groups (e.g. 1,4-cyclohexanedimethanol), high intramolecular mobility (e.g. diethylene glycol) or more accessible primary hydroxyl groups (e.g. ethylene glycol, 2,2-dimethyl-1,3-propanediol).

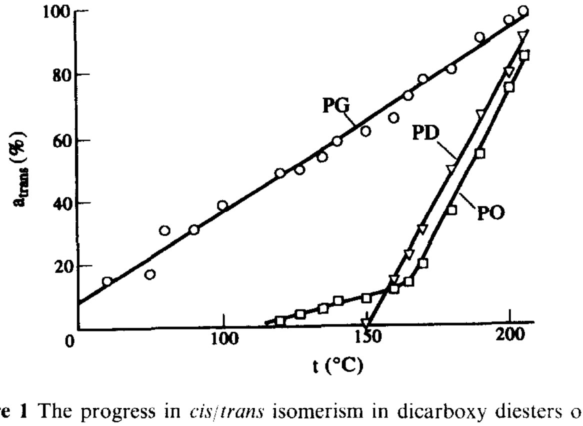


Figure 1 The progress in *cis/trans* isomerism in dicarboxy diesters of maleic anhydride and various diols *versus* reaction temperature

The difference in the isomerization behaviour of PG, PD and PO systems thus appears to be consistent with the chemical structures of the examined diols. As expected, due to steric effects the highest degrees of isomerism are observed for dicarboxy diesters derived from the small molecule of PG exhibiting an enhanced preference in the formation of *trans* isomers[1,2]. Such a preference is evidently lower for PO and PD, which possess distant hydroxyl groups, even though these groups are secondary ones (^{1}H and ^{13}C n.m.r. analyses revealed PO and PD to contain respectively 100 and 85% of secondary hydroxyl groups[6]). The two-step (or nonlinear) character of the plot observed for PO diester may result from a distribution of molecular mass of this diol; the diesters derived from shorter PO chains probably tend to form *trans* isomers at lower temperatures. The high-temperature section of the PO plot exhibits lower *trans* contents (a_{trans}) than those observed for PD. Such behaviour may be attributed mainly to the high molecular mobility of longer PO chains.

Figures 2, 3 and *4* display some representative ^{13}C n.m.r spectra of PG, PD, and PO systems in the CHO, CH_2O and CH_3 regions *versus* temperature. Methine, methylene and methyl carbons were all observed to give rise to several signals. The assignment of the lines was carried out with the aid of DEPT experiments and on the basis of the expected directions and magnitudes of the shifts of the signals due to carbon atoms in the diols upon the reaction with maleic anhydride; the latter was assumed to affect the carbon chemical shifts of hydroxy compounds in a similar fashion as trichloroacetyl isocyanate (TAI)[11]. Some of the lines in *Figure 2* can reasonably be ascribed to the four isomeric forms in which PG dicarboxy diesters can exist: *cis/cis, cis/trans, trans/cis* and *trans/trans*. The remaining signals observed at lower temperatures (up to 80°C) are due to the presence of carboxy hydroxy monoesters. Above 140°C the lines arising from the dicarboxy diesters are overlapped by the signals due to longer sequences; formation of the latter was evidenced by analysing the spectral region of unsaturated carbons[6]. Unlike the PG system, due to the large intramolecular distance between hydroxyl groups, in PD and PO the influence of the other end is negligibly small, making observation of various dicarboxy diester isomers impossible. The chemical structures of the isomers along with chemical shifts of the carbons are listed in *Table 1* and *2*. The assignment of the lines to individual dicarboxy diesters was made by the observation of changes in their intensity with temperature, i.e. with increasing overall content of the *trans* isomers. The effects of *cis–trans* isomerism on the extents and directions of the shifts of the lines due to individual PG, PD and PO carbons are summarized in *Table 3* (note the additivity of the effects and the larger influence experienced by methine as compared with methylene carbons). According to the designations used in *Table 1* for PG dicarboxy diesters, the *cis/trans* isomer for CH

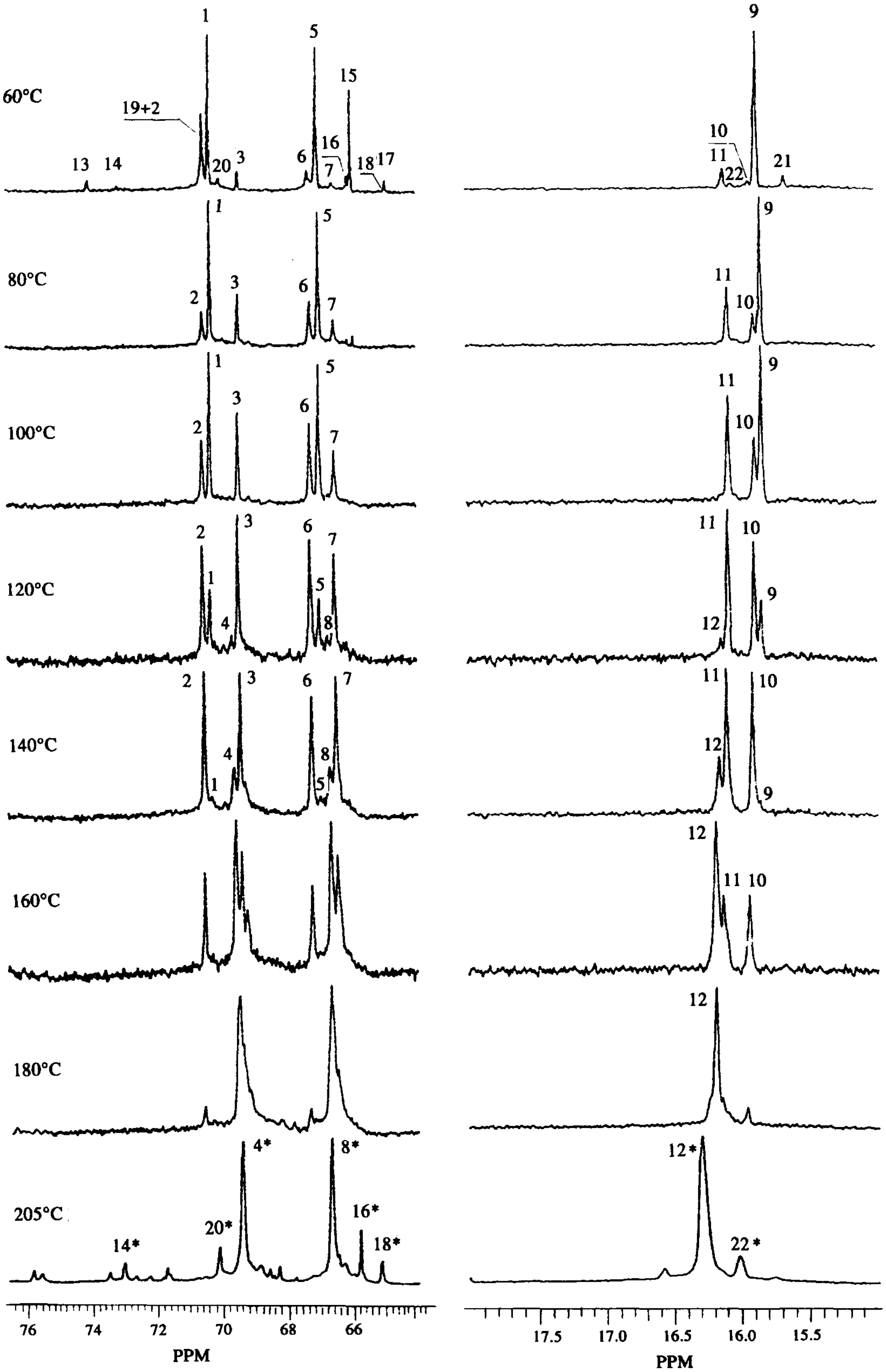


Figure 2 ^{13}C n.m.r. spectra of the products formed in the reaction of 1,2-propylene glycol (PG) with excess amount of maleic anhydride at different temperatures; the bottom spectra refer to corresponding polyester obtained at 205°C. Dicarboxy diesters CH carbons 1–4: *cis/cis* (1), *cis/trans* (2), *trans/cis* (3), *trans/trans* (4). Dicarboxy diesters CH$_2$ carbons 5–8: *cis/cis* (5), *cis/trans* (6), *trans/cis* (7), *trans/trans* (8). Dicarboxy diesters CH$_3$ carbons 9–12: *cis/cis* (9), *cis/trans* (10), *trans/cis* (11), *trans/trans* (12). Carboxy hydroxy monoesters CH carbons 13–16: *cis/-* (13), *trans/-* (14), *-/cis* (15), *-/trans* (16). Carboxy hydroxy monoesters CH$_2$ carbons 17–20: *-/cis* (17), *-/trans* (18), *cis/-* (19), *trans/-* (20). Carboxy hydroxy monoesters CH$_3$ carbons 21–24 (23 and 24 not shown, 18.6 and 18.8 ppm, respectively): *cis/-* (21), *trans/-* (22), *-/cis* (23), *-/trans* (24). 4*, 8* and 12*: carbons in internal fumarate–diol–fumarate sequences and in carboxy-terminated diol–carboxy fumarate polyester chain ends corresponding to *trans* dicarboxy diesters. 14*, 16*, 18*, 20*, 22* and 24* (24*, not shown, 18.8 ppm): carbons in hydroxy-terminated fumarate-diol polyester chain ends corresponding to *trans* carboxy hydroxy monoesters. The unassigned signals in the bottom spectra are due to change branching[5]

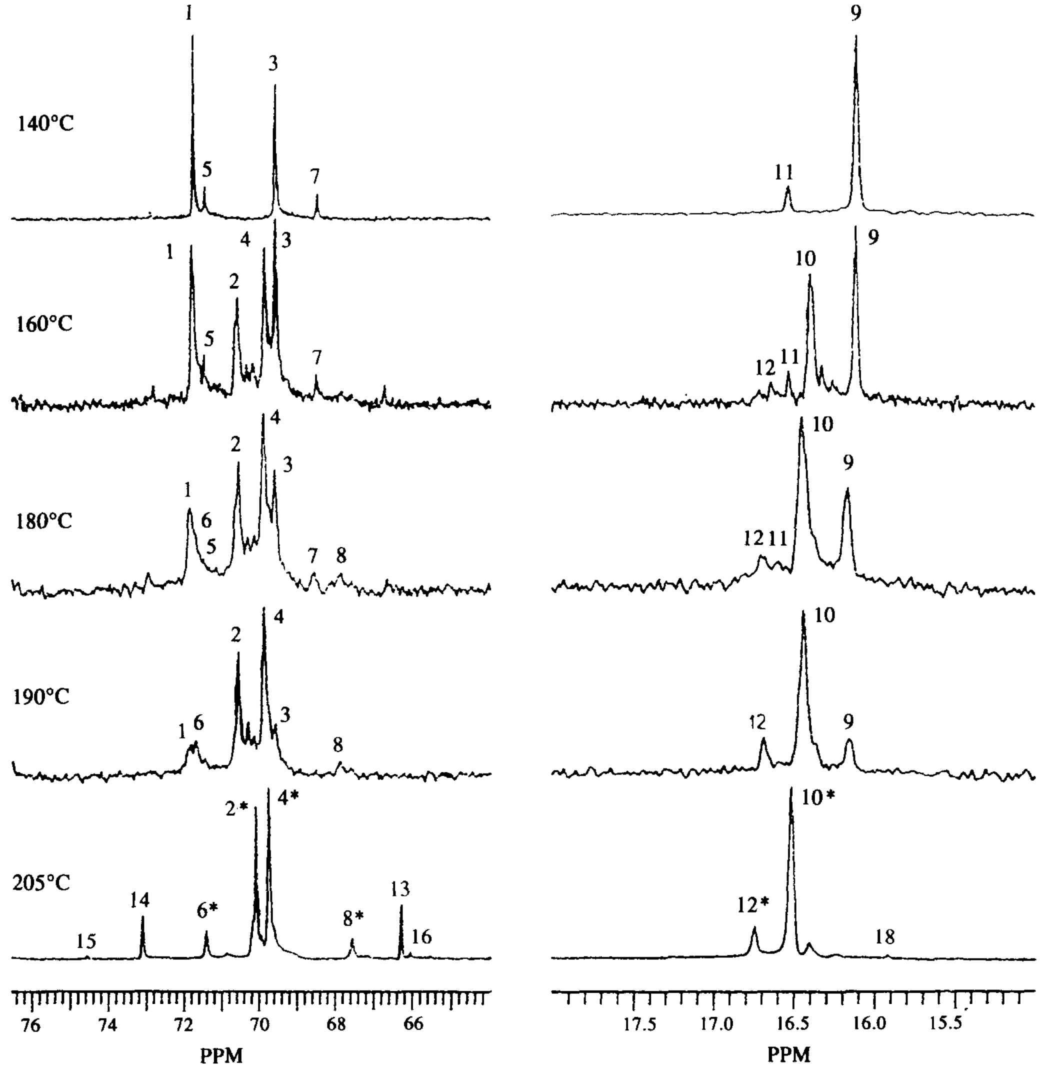


Figure 3 ^{13}C n.m.r. spectra of the products formed in the reaction of 2,2-di(4-hydroxypropoxyphenyl)propane (PD) with excess amount of maleic anhydride at different temperatures; the bottom spectra refer to corresponding polyester obtained at 205°C. CH carbons 1, 2, 5, 6 *cis*(1), *trans* (2), -/*cis* (5), -/*trans* (6). CH_2 carbons 3, 4, 7, 8: -/*cis* (3), -/*trans* (4), *cis* (7), *trans* (8). CH_3 carbons 9–12: *cis* (9), *trans* (10), -/*cis* (11), -/*trans* (12). 2*, 4*, 6*, 8*, 10* and 12*: carbons in internal fumarate–diol–fumarate sequences and in carboxy-terminated diol–carboxyfumarate polyester chain ends corresponding to *trans* carboxy esters. 13–18 (17, not shown, 18.7 ppm): carbons in hydroxy-terminated fumarate–diol polyester chain ends corresponding to unreacted PD[6]

and CH_3 is equivalent to the *trans/cis* isomer for CH_2, while the CH *trans/cis* ≡ CH_3 *trans/cis* ≡ CH_2 *cis/trans*.

Having assigned the resonances of the carbons in individual isomers of PG dicarboxy diesters, the process of isomerism could be monitored by integrating the peak areas. *Figure 5* presents the variations in the relative intensities of the lines arising from the CH (or CH_3) carbons in the different isomers as a function of an overall degree of isomerism pertaining exclusively to dicarboxy diesters. For the reason mentioned above, at higher temperatures the approximate intensity values were obtained by combining the results from different spectral regions. As expected, a reduction in *cis/cis* isomer content accompanied by an increase in the amount of *trans/trans* isomer is observed with increasing overall fumarate content, a_{trans}. However, the *cis/cis* isomer disappears already at $a_{trans} = 0.8$, whereas at lower a_{trans} values (below 0.2) no *trans/trans* isomer is present. The amount of *trans*(CH)/*cis*(CH_2) isomer appears to exceed that of *cis*(CH)/*trans*(CH_2) isomer, which indicates the *cis* to *trans* insomerism to be more favoured at CH (it is worthwhile to note that such observations can be successful only for the model compounds of dicarboxy disester type; in longer sequences the amounts of *trans/cis* and *cis/trans* isomers must be equal to each other).

The experimental data corresponding to *trans/cis*, *cis/trans*, *trans/trans* and *cis/cis* isomers were fitted to the curves described by the following equations:

$$a_{trans/cis} = k_1 a_{trans}(1 - a_{trans})$$

$$a_{cis/trans} = k_2(1 - a_{trans})a_{trans}$$

$$a_{trans/trans} = k_3(a_{trans} - 0.2)^2 \qquad \text{for } 0.2 \le a_{trans} \le 1.0$$

$$a_{cis/cis} = k_4[1-(a_{trans} - 0.2)]^2 \qquad \text{for } 0.0 \le a_{trans} \le 0.8$$

where a_{trans} and $(1 - a_{trans})$ are the overall *trans* and *cis* contents, respectively

The k_1 and k_2 values were found to be about 1.7 and 1.2, respectively. A reverse behaviour was observed for CH_2 carbon signals which is accounted for by the prevalence of *cis*(CH_2)/*trans*(CH) isomer over *trans* (CH_2)/*cis*(CH) isomer in this case. The k_1/k_2 ratio can be considered as a measure of the preference of CH

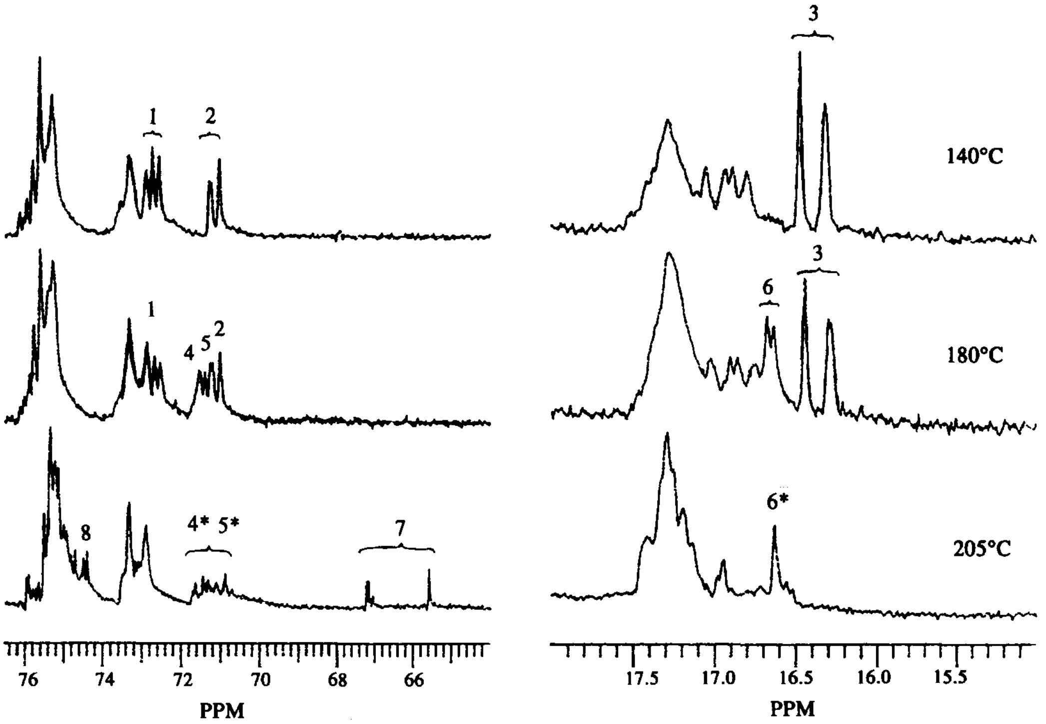


Figure 4 ^{13}C n.m.r. spectra of the products formed in the reaction of oligomer of propylene oxide (PO) with excess amount of maleic anhydride at different temperatures; the bottom spectra refer to corresponding polyester obtained at 205°C; only the assignment of ultimate PO units is given. CH carbons 1, 4: *cis* (1), *trans* (4). CH_2 carbons 2, 5,: -/*cis* (2), -/trans (5). CH_3 carbons 3, 6: *cis* (3), *trans* (6). 4*, 5* and 6*: carbons in internal fumarate–diol–fumarate sequences and in carboxy-terminated diol–carboxyfumarate polyester chain ends corresponding to *trans* carboxy esters. 7–9 (9, not shown, 18.1–18.6 pmm): carbons in hydroxy-terminated fumarate–diol polyester chain ends corresponding to unreacted PO[6]

isomerism over CH_2 isomerism, related to the higher energetic stability of the resulting *trans*(CH)/*cis*(CH_2) form as compared with the *trans*(CH_2)/*cis*(CH) form.

It seems that also the relative magnitudes of the chemical shift changes observed for CH ($\Delta\delta$[CH] = 0.9 ppm) and CH_2 ($\Delta\delta[CH_2]$= 0.6 ppm) resonances (*Table 3*) reflect the difference in the steric conditions promoting the formation of *trans* isomer as well as in the stability gained by the *trans*(CH)/*cis*(CH_2) *versus* the *cis*(CH)/*trans*(CH_2) isomeric form.

For PD and PO systems the *cis–trans* isomeric changes occurring in the directly attached unsaturation-containing units and sensed by the CH, CH_2 and CH_3 carbons (*Figures 3* and *4*, *Tables 2* and *3*) were found to be similar to those for PG (*Figure 1*, *Tables 1* and *3*).

Polyesters

The final values obtained for the diesters at 205°C after 3 h (*Figure 1*) are close to those measured for corresponding polyesters with $n \approx 5$ repeating units (polymerization time: several hours[6]), indicating that most isomerism takes place at the early stages of polycondensation. This observation is in agreement with the findings of Vancsó-Szmercsányi *et al.*[1] and Curtis *et al.*[2]. Moreover, the observed correlation between the structure of the diols and the isomerism of their diesters provides a straightforward explanation of the differences in the *trans* isomer content in the polyesters containing one kind of diol units.

The degrees of isomerism were also determined in previously studied mixed polyesters, i.e. those containing two of three kinds of different diol units. The polymers were abbreviated as M*xyz* with *x*, *y* and *z* being respectively the average amounts of PD, PO and PG units in the chain[6]. As expected, polyesters of M*x*0*z* type exhibit high a_{trans} values (> 95%) as both PD and PG promote the high *trans* content. For M*xy*0 polyesters with block arrangement of PD and PO units, the degrees of isomerism are evidently reduced as compared with the a_{trans} values observed for the corresponding polyesters of the same overall composition containing randomly distributed diol units of these two kinds. High a_{trans} values (94–99%) were found in all mixed polyesters M*xyz*, including PO-rich polymers (M141, M132 and M231) for which noticeable lowering of the degree of isomerism could be expected.

These observations can be explained when assuming that the *trans* content is reduced mainly in internal

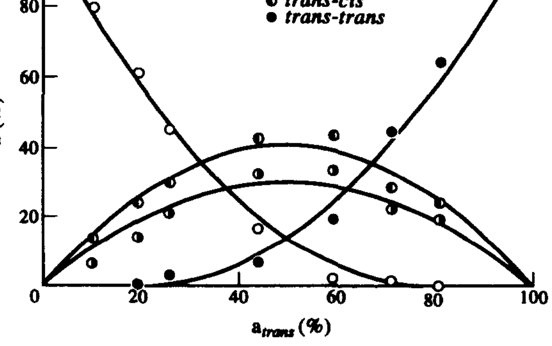
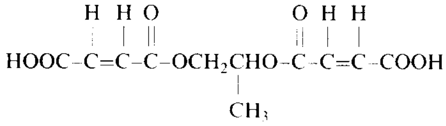
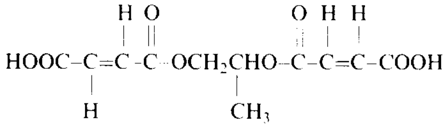
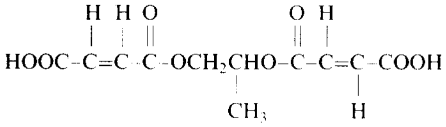
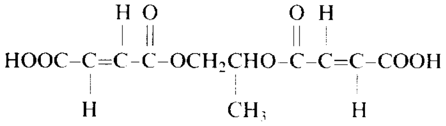
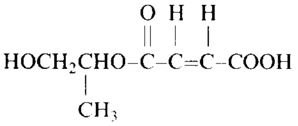
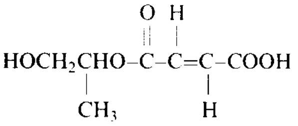
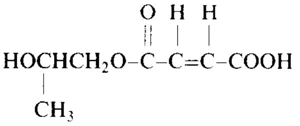
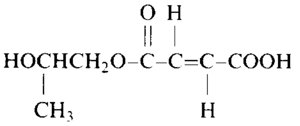


Figure 5 The distribution of isomers of dicarboxy diesters formed in the reaction of maleic anhydride with 1,2-propylene glycol

Table 1 The structures of dicarboxy diesters and carboxy hydroxy monoesters derived from maleic anyhydride and 1,2-propylene glycol (PG), and the ^{13}C chemical shifts of CHO, CHOH, CH_2O, CH_2OH and CH_3 carbons

	Designation, carbon no. and chemical shift (ppm)		
Isomer	CH	CH_2	CH_3
 $HOOC-C=C-C-OCH_2CHO-C-C=C-COOH$	*cis/cis* C1 70.3	*cis/cis* C5 67.0	*cis/cis* C9 15.8
 $HOOC-C=C-C-OCH_2CHO-C-C=C-COOH$	*cis/trans* C2 70.6	*trans/cis* C7 66.4	*cis/trans* C10 15.9
 $HOOC-C=C-C-OCH_2CHO-C-C=C-COOH$	*trans/cis* C3 69.4	*cis/trans* C6 67.3	*trans/cis* C11 16.1
 $HOOC-C=C-C-OCH_2CHO-C-C=C-COOH$	*trans/trans* C4 69.7	*trans/trans* C8 66.7	*trans/trans* C12 16.2
 $HOCH_2CHO-C-C=C-COOH$	*cis/-* C13 74.0	*-/cis* C17 64.8	*cis/-* C21 15.7
 $HOCH_2CHO-C-C=C-COOH$	*trans/-* C14 73.1	*-/trans* C18 65.1	*trans/-* C22 16.0
 $HOCHCH_2O-C-C=C-COOH$	*-/cis* C15 65.9	*cis/-* C19 70.6	*-/cis* C23 18.7
 $HOCHCH_2O-C-C=C-COOH$	*-/trans* C16 66.2	*trans/-* C20 70.0	*-/trans* C24 18.8

PO–fumarate–PO and terminal PO–carboxyfumarate sequences while for mixed PD–fumarate–PO (or PG–fumarate–PO) and terminal PD–carboxyfumarate (or PG–carboxyfumarate) sequences the *trans* isomer will be favoured due to the presence of the diol exhibiting a preference towards the formation of such an isomer. In other words, the degree of isomerism in mixed polyesters depends not only on the relative amounts of individual diols, but also on their arrangement (random or block) along the polymer chain (unless they exhibit similar isomerization behaviour). For block-like distribution, the extent of isomerism should result from the degrees of isomerism and the length of the 'blocks' formed by diverse diols. On the contrary, in the case of random distribution or low content of diols with the weaker tendency to form *trans* isomer, the presence of diols with higher ability to form *trans* isomer should enhance the overall degree of isomerism. The experimental degrees of isomerism were found to be in good agreement with the values calculated when taking into account the amounts of individual diol–fumarate–diol sequences as determined from the compositional sequence distribution according to the previously proposed approach[6].

CONCLUSIONS

Dicarboxy diesters and polyesters derived from maleic anhydride and propylene glycol (PG), an oligomer of propylene oxide (PO) and 2,2-di(4-hydroxypropoxyphenyl)propane (propoxylated dian, PD) exhibit substantial differences in the *cis* to *trans* isomerization behaviour as revealed by n.m.r. spectroscopy. The extent of the isomerism at a given temperature appears to be intimately associated with the chemical structure of the diol units. The double bond isomerism is enhanced in

Table 2 The structures of carboxy esters derived from maleic anhydride and 2,2-di (4-hydroxypropoxyphenyl)propane (PD) or the oligomer of propylene oxide (PO), and the ^{13}C chemical shifts of CHO, CH_2O and CH_3 carbons

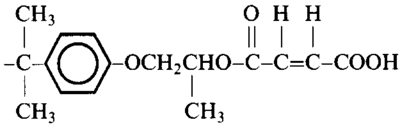
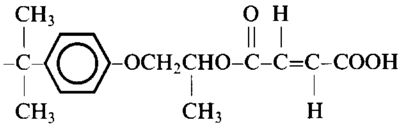
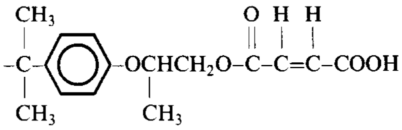
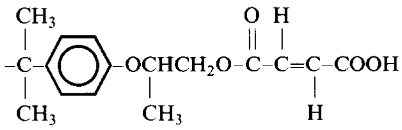
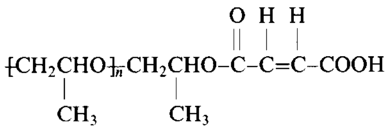
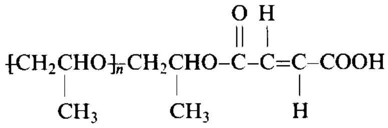
	Designation, carbon no. and chemical shift (ppm)		
Isomer	CH	CH_2	CH_3
	*cis* C1 71.8	-/*cis* C3 69.5	*cis* C9 16.1
	*trans* C2 70.6	-/*trans* C4 69.8	*trans* C10 16.4
	-/*cis* C5 71.4	*cis* C7 68.5	-/*cis* C11 16.5
	-/*trans* C6 71.7	*trans* C8 67.8	-/*trans* C12 16.6
 $\left[CH_2\underset{CH_3}{CH}O\right]_n CH_2\underset{CH_3}{CH}O-\overset{O}{\overset{\|}{C}}-\overset{H}{C}=\overset{H}{C}-COOH$	*cis* C1 72.6–72.8	-/*cis* C2 70.9–71.2	*cis* C3 16.3–16.5
 $\left[CH_2\underset{CH_3}{CH}O\right]_n CH_2\underset{CH_3}{CH}O-\overset{O}{\overset{\|}{C}}-\overset{H}{C}=\underset{H}{C}-COOH$	*trans* C4 71.4–71.6	-/*trans* C5 71.2–71.4	*trans* C6 16.6–16.7

Table 3 The effects of *cis-trans* isomerism on the extents and directions of the chemical shift changes of the lines due to individual PG, PD and PO carbons

Diol	Carbon	Designation	Magnitude of change in chemical shift (ppm)	Direction of change in chemical shift
PG	CH	*cis/cis → trans/cis*	0.9	upfield
		cis/trans → trans/trans	0.9	upfield
		cis/cis → cis/trans	0.3	downfield
		trans/cis → trans/trans	0.3	downfield
		cis/cis → trans/trans	0.6	upfield
	CH_2	*cis/cis → trans/cis*	0.6	upfield
		cis/trans → trans/trans	0.6	upfield
		cis/cis → cis/trans	0.3	downfield
		trans/cis → trans/trans	0.3	downfield
		cis/cis → trans/trans	0.3	upfield
	CH_3	*cis/cis → trans/cis*	0.3	downfield
		cis/trans → trans/trans	0.3	downfield
		cis/cis → cis/trans	0.1	downfield
		trans/cis → trans/trans	0.1	downfield
		cis/cis → trans/trans	0.4	downfield
PD	CH	*cis → trans*	1.2	upfield
		-/*cis* → -/*trans*	0.3	downfield
	CH_2	-/*cis* → -/*trans*	0.3	downfield
		cis → trans	0.7	upfield
	CH_3	*cis → trans*	0.3	downfield
		-/*cis* → -/*trans*	0.1	downfield
PO	CH	*cis → trans*	1.2	upfield
	CH_2	-/*cis* → -/*trans*	0.3	downfield
	CH_3	*cis → trans*	0.3	downfield

the following order: PO<PD<PG. The differences can be explained by considering the influence of various structural factors dicussed in the literature[1,2]. The isomerism is governed by the distance between hydroxyl groups, their type (primary *versus* secondary) and molecular mobility. A presence of a secondary hydroxyl group is decisive in determining the extent of isomerism of PG systems. The *trans* content of PO-containing systems is influenced by a high mobility combined with a larger distance between hydroxyl groups, whereas the wider separation of hydroxyl groups seems to affect the behavior of PD systems. The degree of isomerism of mixed polyesters is determined by the overall composition (kinds and relative amounts of diols) and (at least partially) modified by the distribution of diol units along the chain.

ACKNOWLEDGEMENT

The author is indebted to M.Sc. student Antoni Kotas for preparation of samples.

REFERENCES

1 Vancsó-Szmercsányi, I., Maros-Créger, K. and Makay-Bödi, E. *J. Polym. Sci.* 1961, **53**, 241

2 Curtis, L. G., Edwards, D. L., Simons, R. M., Trent, P. J. and Von Bramler, P. T. *Ind. Eng. Chem. Prod. Res. Dev.* 1964, **3**, 218

3 Bellenger, V., Mortaigne, D., Grenier-Loustalot, M. F. and Verdu, J. *J. Appl. Polym. Sci.* 1992, **44**, 643

4 Klyuchnikov, V. N., Filippenko, D. M.-Ya., Slonim, I. Ya., Urman, Ya. G., Bulai, A. Kh., Strokova, L. D. and Sedov, L. N. *Vysokomol. Soedin.* 1980, **22**, 2747

5 Judas, D., Fradet, A. and Maréchal, E. *Makromol. Chem.* 1984, **185**, 2583

6 Grobelny, J. and Kotas, A. *Polymer* 1995, **36**, 1363

7 Campbell, I. D., Dobson, C. D., Willims, R. J. and Xavier, J. *J. Magn. Reson.* 1973, **11**, 172

8 Lindon, J. C. and Ferrige, A.G. *Prog. Nucl. Magn. Reson. Spectrosc.* 1980, **14**, 27

9 Kupka, T., Pacha, J. and Dzięgielewski, J. O. *Magn. Reson. Chem.* 1989, **27**, 21

10 VXR-Series. Systems Operation Manual. NMR Spectrometer Systems, Pub. No. 87-178214-00 (Rev. C0187), Varian, Palo Alto, USA

11 Bose, K. and Srinivasan, P. R. *Tetrahedron* 1975, **31**, 3025