Elimination of three-dimensional order in thermotropic copolyesters*

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Previous work has shown that crystallization is suppressed in some thermotropic copolyesters containing between five and seven different units of different types (rod-like, crankshaft and rigid angular). However, no general rules for design of such copolymers could be formulated. It is now found that crystallizability of random copolyesters is related to probabilities of tetrads forming crystallizable sequences. Relationships for calculating the probabilities of such tetrads in random multicomponent copolyesters are derived. A criterion for design of non-crystalline copolyesters is formulated.

(Keywords: thermotropic polyesters; crystallization; unit sequences)

INTRODUCTION

Over the past 15 years the main-chain nematogenic polymers, particularly aromatic copolyesters, have received much attention owing to their potential applications as high-performance engineering materials[1-3] and as materials for production of high-performance fibres[4]. For these applications it is desirable to maintain crystallizability. However, for the utilization of nematogenic polymers as processing aids for linear flexible-chain polymers, it appears to be desirable to suppress the crystallization[5], since then the non-crystalline nematic glass transforms directly into a nematic melt above the glass transition temperature. Thus, the flow temperature is much lower than in the case of semicrystalline nematogenic polymers[6].

In the case of linear flexible-chain polymers it is easy to eliminate the formation of crystalline structures by copolymerization[7]. In contrast, in nematogenic copolymers the capability to crystallize is very persistent, since very thin crystallites are feasible[8-10], and both imperfect crystalline structures[11,12] and non-periodic layer (NPL) crystals[13,14] can be formed.

It has been established that the use of substituted aromatic units can result in non-crystalline nematogenic copolyesters[5,15]. We have explored another approach, based on increasing the number of unsubstituted aromatic units[6]. The constituent units (*Table 1*) contain rod-like 1,4-phenylene and 4,4'-biphenylene (abbreviated P and PP, respectively), crankshaft 2,6-naphthylene (N) and rigid angular 1,3-phenylene (M) groups. Using wide-angle X-ray scattering (WAXS), differential scanning calorimetry (d.s.c.) and onset of flow observed by hot-stage microscopy as the criteria, five of the copolymers were classified as non-crystalline; they contained between five and seven units of different types (*Table 2*). Subsequently, these non-crystalline copolymers were subjected to extensive heat treatments, which for four of them resulted in some crystallization, evidenced by d.s.c. and flow behaviour; only copolymer XVI containing seven different units did not crystallize[16].

Hitherto, the choice of the composition for suppressing the crystallization has been entirely empirical. The purpose of this work is to provide a rational framework for design of non-crystalline nematogenic copolyesters. Since crystallization can take place only if sufficiently long sequences of units capable of forming a crystalline structure are present in the polymer chains in sufficient number, the statistics of unit sequences in multicomponent copolyesters is evaluated. Next, criteria of crystallizability, based on the crystallization behaviour of 'simple' copolymers, are considered. Finally, the validity of these criteria is tested using the copolymers listed in *Table 2*.

UNIT SEQUENCES IN MULTICOMPONENT RANDOM COPOLYESTERS

The problem of unit sequences in copolymers formed by chain polymerizations has received much attention[17,18], and resulted in development of models of ever-increasing complexity (terminal, penultimate, pen-penultimate, complex participation). In contrast, copolycondensation has been the subject of only a few fundamental studies, dealing mostly with only two or three reactants[19]. In comparison with chain copolymerizations, copolycondensations are much less interesting; provided that the reaction mixture remains homogeneous, the interchange reactions, such as transesterification, will ultimately cause randomization even if the copolycondensate is initially non-random, owing to the different reactivities of the monomers.

The treatment of multicomponent copolyesters presented here is limited to random chains. This is justified, unless high-melting oligomeric species (e.g. poly(4-oxybenzoate)) precipitate from the reaction mixture. Furthermore, at this stage we only consider chains of infinite length.

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Incorporation of end-groups does not present any fundamental difficulties, but it results in increased complexity of the resulting relationships.

In a general case the copolyester chain consists of units resulting from oxyacids, diols and diacids. Since the units originating from oxyacids are asymmetrical, the oppositely directed versions must be viewed as different entities occurring in the chain with equal probabilities. Thus, the probabilities P_1 of finding individual units in the chain are related to the molar fractions as follows:

$$\begin{aligned} P_1\{\mathrm{OA}_i\mathrm{CO}\} &= P_1\{\mathrm{COA}_i\mathrm{O}\} = [\mathrm{OA}_i\mathrm{CO}]/2 \\ P_1\{\mathrm{OA}_i\mathrm{O}\} &= [\mathrm{OA}_i\mathrm{O}] \\ P_1\{\mathrm{COA}_i\mathrm{CO}\} &= [\mathrm{COA}_i\mathrm{CO}] \end{aligned} \qquad (1)$$

where A_i represents generally an aromatic, heterocyclic or aliphatic group. For the copolymers investigated (*Table 2*), A_i = P, PP, N or M.

It is assumed that the unit sequences in the multicomponent copolyesters obey Markov chain statistics of order 1. The probability of finding a diad consisting of specific units Z_1 and Z_2 is therefore:

$$P_2\{Z_1Z_2\} = P_1\{Z_1\}P(Z_1/Z_2)$$

where $P(Z_1/Z_2)$ is the conditional probability that unit Z_2 follows unit Z_1. For a specific sequence consisting of m units Z_1 to Z_m we get:

$$P_m\{Z_1 \ldots Z_m\} = P_1\{Z_1\}P(Z_1/Z_2) \ldots P(Z_{m-1}/Z_m) \qquad (2)$$

The units Z can be of any type (i.e. $\mathrm{OA}_i\mathrm{CO}$, $\mathrm{COA}_i\mathrm{O}$, $\mathrm{OA}_i\mathrm{O}$, $\mathrm{COA}_i\mathrm{CO}$) and the choice of groups A_i is unrestricted.

Next we need to consider the conditional probabilities. Let q represent either O or CO. Obviously:

$$P(\mathrm{qA}_i\mathrm{O}/\mathrm{OA}_j\mathrm{q}) = 0 \qquad (3a)$$

$$P(\mathrm{qA}_i\mathrm{CO}/\mathrm{COA}_j\mathrm{q}) = 0 \qquad (3b)$$

Since in an infinite chain each unit must be followed by another unit we get:

$$P(\mathrm{qA}_i\mathrm{O}/\mathrm{COA}_j\mathrm{q}) = 2P_1\{\mathrm{COA}_j\mathrm{q}\} \qquad (4a)$$

$$P(\mathrm{qA}_i\mathrm{CO}/\mathrm{OA}_j\mathrm{q}) = 2P_1\{\mathrm{OA}_j\mathrm{q}\} \qquad (4b)$$

Note that for a given aromatic group (i.e. $i=j$), equations (3) and (4) define 16 conditional probabilities; for two types of aromatic groups they define 64 conditional probabilities; and for n types of aromatic groups this increases to $(4n)^2$. Using these conditional probabilities together with equations (1) and (2), the probability of any specified sequence of units can be calculated.

For the purpose of this work it is also important to consider less specific sequences, namely those where the direction of ester groups is arbitrary, but where all the aromatic groups are identical. Thus, we wish to evaluate the probabilities $P_m\{(\mathrm{qA}_x\mathrm{q})_m\}$, where A_x is a specific aromatic group, for instance 1,4-phenylene (i.e. A_x = P). For this task it is convenient to use matrices. It is found that:

$$P_m\{(\mathrm{qA}_x\mathrm{q})_m\} = (\boldsymbol{P}_{xx}{}^{m-1}\,\boldsymbol{U})^{\mathrm{T}}\boldsymbol{C} \qquad (5)$$

Table 1 Units employed in multicomponent copolyesters

Type	Unit	Abbreviation
Rod-like	4-Oxybenzoyl	OPCO
	1,4-Phenylenedioxy	OPO
	Terephthaloyl	COPCO
	4,4′-Biphenylenedioxy	OPPO
Crankshaft	6-Oxy-2-naphthoyl	ONCO
Rigid angular	3-Oxybenzoyl	OMCO
	1,3-Phenylenedioxy	OMO
	Isophthaloyl	COMCO

Table 2 Composition and crystallization behaviour of multicomponent copolyesters (abbreviations as in *Table 1*)

	Amount of unit (mole fraction × 100)								
Polymer	OPCO	OPO	COPCO	OPPO	ONCO	OMCO	OMO	COMCO	Behaviour[a]
I	25	0	0	25	25	0	0	25	(i)
II	30	10	10	25	0	0	0	25	(i)
III	40	0	10	25	0	10	0	15	(ii)
IV	15	0	10	25	25	10	0	15	(iv)
V	20	0	10	40	0	0	0	30	(i)
VI	30	0	10	30	0	10	0	20	(i)
VII	0	0	20	40	10	10	0	20	(i)
VIII	10	0	0	20	40	10	0	20	(iv)
IX	50	10	10	0	0	10	10	10	(i)
X	50	0	10	10	0	10	10	10	(ii)
XI	30	10	10	20	0	10	0	20	(ii)
XII	10	0	10	30	20	10	0	20	(i)
XIII	0	10	10	20	30	10	0	20	(iv)
XIV	0	10	10	0	50	10	10	10	(iv)
XV	25	10	10	0	25	10	10	10	(iii)
XVI	10	10	10	0	40	10	10	10	(v)

[a] Key:
(i) Semicrystalline according to WAXS, d.s.c. and flow behaviour
(ii) Semicrystalline according to d.s.c. and flow behaviour
(iii) Presence of ordered structures suggested by flow behaviour only
(iv) Non-crystalline, but extensive heat treatments resulted in crystallization evidenced by d.s.c. and flow behaviour
(v) Non-crystalline even after extensive heat treatment

where the matrix of conditional probabilities is

$$\boldsymbol{P}_{xx}=\begin{pmatrix} [\mathrm{OA}_x\mathrm{CO}] & 0 & 2[\mathrm{OA}_x\mathrm{O}] & 0 \\ 0 & [\mathrm{OA}_x\mathrm{CO}] & 0 & 2[\mathrm{COA}_x\mathrm{CO}] \\ 0 & [\mathrm{OA}_x\mathrm{CO}] & 0 & 2[\mathrm{COA}_x\mathrm{CO}] \\ [\mathrm{OA}_x\mathrm{CO}] & 0 & 2[\mathrm{OA}_x\mathrm{O}] & 0 \end{pmatrix} \tag{6}$$

U is a 4×1 unit column vector, and the column vector C, replacing $P_1\{Z_1\}$ in equation (2), is defined as:

$$C=\begin{pmatrix} [\mathrm{OA}_x\mathrm{CO}]/2 \\ [\mathrm{OA}_x\mathrm{CO}]/2 \\ [\mathrm{OA}_x\mathrm{O}] \\ [\mathrm{COA}_x\mathrm{CO}] \end{pmatrix} \tag{7}$$

The probabilities for diads, triads and tetrads obtained from equation (5) are given in the Appendix.

Using this approach, it is also possible to evaluate the probabilities of sequences where the direction of ester groups is arbitrary and where the aromatic groups are of two or more specified types; for example A_x is 1,4-phenylene and/or 4,4′-biphenylene (i.e. $A_x = P \cup PP$). The concentrations in equations (6) and (7) are then sums of concentrations of the appropriate units (e.g. $[\mathrm{OA}_x\mathrm{O}] = [\mathrm{OPO}] + [\mathrm{OPPO}]$).

In order to evaluate the probabilities of sequences where the direction of ester groups is arbitrary, but where two kinds of aromatic groups follow a specified order (e.g. qPqqNqqNqqPq, where qq represents either O CO or CO O), it is necessary to use a 16×16 matrix of conditional probabilities. This work, which is relevant to the occurrence of NPL crystals, is in progress.

CRITERIA OF CRYSTALLIZABILITY

As already noted, the crystallizability will be affected by the probability of the sequences with lengths required for the formation of stable crystallites. Unfortunately, this length corresponding to the critical thickness of the crystallites cannot be derived theoretically since the relevant thermodynamic parameters[7] (equilibrium melting temperature, heat of fusion and the interfacial energies) are not known. It is doubtful whether these parameters can ever be determined for the crystal structures occurring in nematogenic copolyesters. We are therefore forced to base the criteria of crystallizability on deductions from the crystallization behaviour of 'simple' nematogenic copolyesters, namely poly(4-oxybenzoate-*co*-1,4-phenylene isophthalate)s, consisting of OPCO, OPO and COMCO units[9–11,20]. It has been established that crystallization of the copolymers where $[\mathrm{OPCO}] \geqslant 0.60$ (i.e. $[\mathrm{COMCO}] = [\mathrm{OPO}] \leqslant 0.20$) results in an imperfect poly(4-oxybenzoate) structure consisting of OPCO and OPO units[11,20]; here it is referred to as type A′ structure. In the copolymers where $[\mathrm{OPCO}] \leqslant 0.40$ (i.e. $[\mathrm{COMCO}] = [\mathrm{OPO}] \geqslant 0.30$), structures consisting of (OPO–COMCO) sequences prevailed; two forms, referred to as types B and C respectively, have been identified[9–11,20]. However, for the purpose of defining the criteria of crystallizability, the behaviour of the copolymer where $[\mathrm{OPCO}] = 0.50$ is most instructive, since this copolymer represents a borderline case. Blundell *et al.*[20] classified the as-made material as 'amorphous', but after melt processing they observed the type C structure. Erdemir *et al.*[11] found that the WAXS patterns of fibres melt-spun from nematic mesophase did not show any sharp reflections. However, the d.s.c. curve showed a melting endotherm at around 375°C and, consequently, these fibres cannot be classified as non-crystalline. Annealing at 335°C resulted in a WAXS pattern of the type A′ structure. In contrast, annealing at 250–280°C resulted in formation of the type C structure. The crystallinity was low and the crystallite thickness obtained from a meridional reflection was only about 2 nm, which corresponds to less than four constituent units[9]. These results suggest that the probability of tetrads of the appropriate sequences should be suitable for assessment of crystallizability. We therefore need to consider the critical values of the probabilities of such tetrads.

Since the reaction mixture must be stoichiometrically balanced, the probability of any specific sequence of units is equal to the probability of the corresponding oppositely directed sequence, i.e.

$$P_m\{Z_1 \ldots Z_m\} = P_m\{Z_m \ldots Z_1\} \tag{8}$$

Hence, for the consideration of the critical levels of probabilities, the value calculated for any specific sequence must be doubled.

The value for tetrads of 4-oxybenzoyl units in poly(4-oxybenzoate-*co*-1,4-phenylene terephthalate) where $[\mathrm{OPCO}] = 0.50$ is $2P_4\{(\mathrm{OPCO})_4\} = 0.0625$; for sequences consisting of 1,4-phenylene groups joined together by ester groups whose direction is arbitrary we get $P_4\{(\mathrm{qPq})_4\} = 0.1875$. The probability of tetrads with alternating OPO and COMCO units, relevant to formation of B or C type structures, is $2P_4\{(\mathrm{OPO\,COMCO})_2\} = 0.0625$. These results suggest that the critical level of probabilities of tetrads required for crystallizability is about 0.06.

Figure 1 shows the probabilities of tetrads discussed

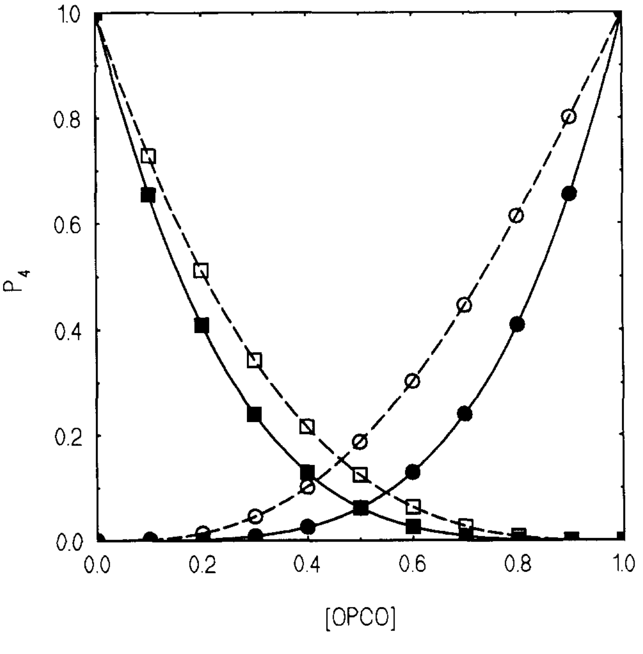

Figure 1 Probabilities of tetrads in poly(4-oxybenzoate-*co*-1,4-phenylene isophthalate)s: (●) $(\mathrm{OPCO})_4$ and $(\mathrm{COPO})_4$; (○) $(\mathrm{qPq})_4$; (■) $(\mathrm{OPO\,COMCO})_2$ and $(\mathrm{COMCO\,OPO})_2$; (□) (qPO COMCO OPO COMCO) and (COMCO OPO COMCO OPq)

above for the whole composition range of poly(4-oxybenzoate-*co*-1,4-phenylene isophthalate)s. In addition, data for the probabilities of tetrads where the units containing 1,4-phenylene group alternate with those containing 1,3-phenylene group are also shown. These results reflect the observed crystallization behaviour, i.e. formation of type B or C structures for $[\mathrm{OPCO}]\leqslant 0.40$ and type A′ structure for $[\mathrm{OPCO}]\geqslant 0.60$, as well as the borderline behaviour of the copolymer where $[\mathrm{OPCO}]=0.50$.

PROBABILITIES OF TETRADS IN MULTICOMPONENT COPOLYESTERS

The validity of the suggested criterion of crystallizability was tested using the multicomponent copolyesters listed in *Table 2*. First, the tetrads corresponding to notional parent homopolymers consisting of identical units (OPCO or ONCO) or of alternating units (e.g. OPPO and COMCO) were considered. As already explained, the calculated probability values (equation (2)) were doubled to account for the corresponding oppositely directed sequences. The maximum values obtained for each copolymer are given in *Table 3*; where two identical maximum values were obtained for different sequences in a given copolymer, the sequence with the higher content of rigid units is listed since it is expected to exhibit a higher crystallizability. Secondly, the probabilities of tetrads of units containing aromatic groups of a given type or types were evaluated (equations (5)–(7) and Appendix); see *Table 4*.

Out of 10 copolymers classified as semicrystalline either by both WAXS and d.s.c. (category (i)) or by d.s.c. only (category (ii)), nine exceeded the critical value of probability either for specific tetrads (*Table 3*) or for sequences $(\mathrm{qA}_x\mathrm{q})_4$ where $\mathrm{A}_x=\mathrm{P}$ or $\mathrm{A}_x=\mathrm{P}\cup\mathrm{PP}$ (*Table 4*). Only copolymer XII (category (i)) did not reach the critical value for any of the sequences considered; the maximum value (0.0576) was calculated for tetrads consisting of OPPO and COMCO units (*Table 3*). It is worth noting that, owing to the presence of 4,4′-biphenylene group in the OPPO units, these tetrads are longer than the tetrads of units with a single benzene ring upon whose behaviour the choice of the critical value is based.

Table 3 Maximum probabilities of tetrads, P_4, corresponding to notional parent homopolymers consisting of (a) single unit and (b) alternating units; for key explaining the crystallization behaviour and for concentrations of the constituent units, see *Table 2*

		(a)		(b)	
Polymer	Behaviour	$2P_4$	Unit	$2P_4$	Units
I	(i)	0.0039	OPCO	0.0625^a	OPPO COMCO
II	(i)	0.0081	OPCO	0.0625^a	OPPO COMCO
III	(ii)	0.0256	OPCO	0.0225	OPPO COMCO
IV	(iv)	0.0039	ONCO	0.0225	OPPO COMCO
V	(i)	0.0016	OPCO	0.2304^a	OPPO COMCO
VI	(i)	0.0081	OPCO	0.0576	OPPO COMCO
VII	(i)	0.0001	ONCO	0.1024^a	OPPO COPCO
VIII	(iv)	0.0256	ONCO	0.0256	OPPO COMCO
IX	(i)	0.0625^a	OPCO	0.0016	OPO COPCO
X	(ii)	0.0625^a	OPCO	0.0016	OPPO COPCO
XI	(ii)	0.0081	OPCO	0.0256	OPPO COMCO
XII	(i)	0.0016	ONCO	0.0576	OPPO COMCO
XIII	(iv)	0.0081	ONCO	0.0256	OPPO COMCO
XIV	(iv)	0.0625^a	ONCO	0.0016	OPO COPCO
XV	(iii)	0.0039	OPCO	0.0016	OPO COPCO
XVI	(v)	0.0256	ONCO	0.0016	OPO COPCO

^{a} Exceeding the suggested critical value

Table 4 Probabilities of tetrads of units containing specified aromatic group(s); for key explaining the crystallization behaviour, see *Table 2*

		$P_4\{(\mathrm{qA}_x\mathrm{q})_4\}$		
Polymer	Behaviour	$\mathrm{A}_x=\mathrm{P}$	$\mathrm{A}_x=\mathrm{P}\cup\mathrm{PP}$	$\mathrm{A}_x=\mathrm{P}\cup\mathrm{N}$
I	(i)	0.0039	0.0195	0.0625^a
II	(i)	0.0625^a	0.2099^a	0.0625^a
III	(ii)	0.0512	0.4028^a	0.0512
IV	(iv)	0.0019	0.0497	0.0512
V	(i)	0.0048	0.1456^a	0.0048
VI	(i)	0.0189	0.1791^a	0.0189
VII	(i)	0.0000	0.1024^a	0.0009
VIII	(iv)	0.0001	0.0009	0.0625^a
IX	(i)	0.2401^a	0.2401^a	0.2401^a
X	(ii)	0.1125^a	0.2401^a	0.1125^a
XI	(ii)	0.0625^a	0.1791^a	0.0625^a
XII	(i)	0.0005	0.0425	0.0189
XIII	(iv)	0.0016	0.0144	0.0625^a
XIV	(iv)	0.0016	0.0016	0.2401^a
XV	(iii)	0.0410	0.0410	0.2401^a
XVI	(v)	0.0081	0.0081	0.2401^a

^{a} Exceeding the suggested critical value

The copolymer XV representing a borderline crystallization behaviour (category (iii)) reached the probability of 0.0410 for $(\mathrm{qPq})_4$ sequences. Amongst the materials that were non-crystalline when synthesized (category (iv)), only the copolymer XIV exceeded the critical value, giving $2P_4\{(\mathrm{ONCO})_4\}=0.0625$. The maximum value for copolymer XVI, which did not crystallize even after extended heat treatment[16] (category (v)), was less than half of the critical value ($2P_4\{(\mathrm{ONCO})_4\}=0.0256$).

These results show that the suggested criterion of crystallizability, based on the behaviour of poly(4-oxybenzoate-*co*-1,4-phenylene isophthalate)s is reasonable; however, the range of probabilities between 0.04 and 0.06 should be considered as borderline, where the crystallization behaviour is affected by the nature of the tetrads. It appears that the critical level for regular tetrads containing longer OPPO units is less than 0.06 (see copolymer XII); in contrast a higher probability of tetrads consisting of crankshaft ONCO units may be acceptable (see copolymer XIV with $[\mathrm{ONCO}]=0.50$, $2P_4\{(\mathrm{ONCO})_4\}=0.0625$).

Table 4 also shows the probabilities of tetrads $P_4\{(\mathrm{qA}_x\mathrm{q})_4\}$ where $\mathrm{A}_x=\mathrm{P}\cup\mathrm{N}$. It is noted that the critical value was exceeded for three copolymers of category (iv). Moreover, a very high probability value (0.2401) was obtained for copolymer XVI, which did not crystallize after an extended heat treatment (category (v)). It is therefore concluded that random sequences of units containing 1,4-phenylene and 2,6-naphthylene groups are not crystallizable. Consequently, when crystallization occurs in random copolymers consisting of rod-like and crankshaft units (e.g. poly(4-oxybenzoate-*co*-2,6-oxynaphthoate)s), it must be primarily due to formation of NPL crystals with matching unit sequences[13,14] rather than to formation of structures with random sequences of these units[21]. Evaluation of probabilities of ordered sequences required for formation of NPL crystals in multicomponent copolyesters is in progress.

CONCLUSIONS

The calculated probabilities of tetrads forming crystallizable sequences yield a rational basis for assessment of crystallizability of thermotropic liquid-crystalline copolyesters. Obviously, in order to suppress crystallization, the probabilities of all such tetrads should be as low as possible. Regarding the tetrads of specific units, this is achieved by using low concentrations of the corresponding monomer or monomers. The probabilities of crystallizable tetrads of units containing aromatic groups of a given type or types can be reduced using a stoichiometrically unbalanced mixture of the relevant monomers.

When these probabilities exceed a critical value, crystallization takes place. The observed crystallization behaviour shows that the critical value is between 0.05 and 0.06, depending somewhat on the nature of the crystallizable sequences. However, a limit of 0.04 is considered a safe criterion for the design of non-crystalline copolyesters.

It has been established that random sequences of units containing 1,4-phenylene and 2,6-naphthylene groups are not crystallizable. This supports the view that crystallization in random copolymers consisting of such units is usually due to the formation of NPL crystals.

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APPENDIX

Probability of sequences of units of specified type(s)

The probabilities $P_m\{(qA_xq)_m\}$ are obtained from equations (5)–(7). The solutions for $m=2$, 3 and 4 are given here. Let:

$$[A_x]=[OA_xCO]+[OA_xO]+[COA_xCO]$$

and

$$a=[OA_xCO]/[A_x]$$
$$b=[OA_xO]/[A_x]$$
$$c=[COA_xCO]/[A_x]$$

Then:

$$P_m\{(qA_xq)_m\}=[A_x]^m B_m$$

where

$$B_2=a^2+2a(b+c)+4bc$$
$$B_3=a^3+3a^2(b+c)+12abc+4bc(b+c)$$
$$B_4=a^4+4a^3(b+c)+24a^2bc+16abc(b+c)+16b^2c^2$$

Note that if the selected set of units is balanced with respect to the functional groups ($[OA_xO]=[COA_xCO]$, i.e. $b=c$), then:

$$B_2=B_3=B_4=1$$

Obviously, for $a=b=0$, $c=1$, or $a=c=0$, $b=1$:

$$B_2=B_3=B_4=0$$