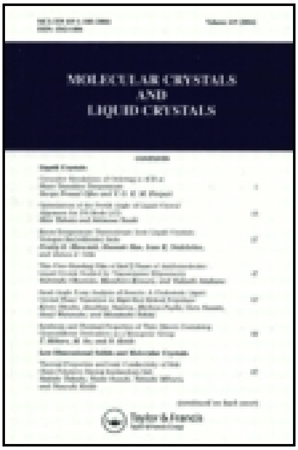

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Molecular Mass Dependemce of Properties in Selected Poly/2-Alkyl-1,4-Phenylene Terephthalate/s

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MOLECULAR MASS DEPENDENCE OF PROPERTIES IN SELECTED POLY/2-ALKYL-1,4-PHENYLENE TEREPHTHALATE/S

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Abstract The properties of selected model compounds, oligomers and polymers consisting of rod like molecule backbones and flexible pendant alkyl groups, were discussed.

INTRODUCTION

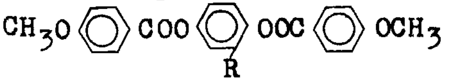
At investigation of polymeric liquid crystals(PLCs) main interest was paid to the relationships between structure and liquid crystalline(LC) behaviour, while the influence of molecular mass(M) was seldom considered. More frequently the LC behaviour of PLCs was compared with low M model compounds.

Blumstein et.al.[1] presented a detailed study of the M influence on a series of main chain PLCs containing flexible alkyl spacers.

Ballauff et.al.[2] described the behaviour of main chain rigid rod oligomers of 4-hydroxybenzoic acid terminated with phenyl groups, reporting that at M=558 the oligomer melts at 224°C forming an isotropic melt at 400°C. Kricheldorf and Schwarz[3] showed that the formation of a LC phase at further increase of M to 1000-1500 for such oligomers was not possible. No melting was observed below 400°C, however a solid-solid transition at temperature slightly exceeding 300°C took place.

The depression of transition temperatures by a lateral substitution of the rigid chains enables the study of LC behaviour for oligomers and polymers.

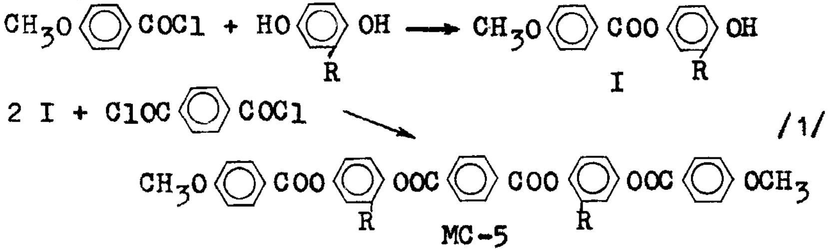
Low M compounds of the general formula given below, were studied for many substituents including alkyl groups[4]. The latter will be discussed here and abreviated as MC-3.



$CH_3O\langle\bigcirc\rangle COO\underset{R}{\langle\bigcirc\rangle}OOC\langle\bigcirc\rangle OCH_3$

SYNTHESIS

Model compounds MC-5, i.e. Bis[2-alkyl-4/4-methoxybenzoyloxy/] terephthalates have been synthesized as presented:



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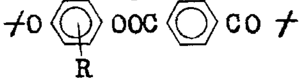
MC-5

The detailed synthesis will be described elsewhere.

Oligomers and polymers of the general structure have been synthesized in polycondensation reactions already described[5,6].



$\not{}\,O\underset{R}{\langle\bigcirc\rangle}OOC\langle\bigcirc\rangle CO\,\not{}$

Their M was controlled by nonequimolar amounts of monomers used and by additional solid state polycondensation. The entire range of samples investigated enclosed model compounds from M~ 400 to polymers of inherent viscosity (I.V.) up to 6 dl/g.

PROPERTIES

Solubility

The samples solubility worstened with the increase of M. MC-3, MC-5 and oligomers of M ⟨1500 were soluble in $CHCl_3$ and CH_2Cl_2 at ambient. Higher M oligomers and polymers bearing larger alkyl substituents (AS) were soluble in hot $Cl_2/CH_2/_2Cl_2$ but formed gels when cooled down below 80°C. All samples were soluble in hot chlorinated phenols forming stable solutions at cold.

Phase transitions

The MC-3 and MC-5 after crystallization from ethanol showed sharp melting points, while oligomers of $M<1500$ exhibited melting at a little broader temperature range Oligomers of $M>1500$ and lower M polymers precipitated during the solution polycondensation, as noncrystalline solids which did not show regular melting and could not be crystallized without change of their M. Higher M polymers formed crystalline structures, however multiple peaks in their X-ray diffractograms could be observed only when the polymers were thermally crystallized for 20-40 hours. It should be noted, that the morphology of the low M model compounds and oligomers seems to be different of that of higher M polymers. In samples of moderate M in the order of few thousands /I.V.=0.2-1.dl/g/ no clear signs of crystallinity could be observed at DSC or X-ray studies.

Isotropisation could be detected for the lower M samples and for polymers bearing long ASs at both, the microscopic and DSC studies. Polymers substituted with short ASs and those of high M did not show isotropisation below their decomposition. It is characteristic that the T_i is strongly dependent on M at lower M, while at higher M this relationship tends to level off. Phase transition data are compiled in Table 1, while the dependence of T_i on M is presented in Figure 1.

Mesophase characteristics

All samples studied formed mesophases, the MC-3 showed monotropic behaviour, while all higher M samples were enantiotropic with a mesophase stability increasing with M. The textures, which were schlieren nematic for the MC-3 and MC-5 melts, changed to more complicated with the increase of M although in polymers of higher M threaded nematic textures were observed[6].

Table 1 Phase transition data for the n-octyl substituted samples.

Sample	$\overline{Mn}$	IV (dl/g)	Melting point (°C)	Melting entropy^x (J/mol•K)	Isotropisation temp. (°C)	Isotropisation entropy^x (J/mol•K)
MC-3	463	-	82	-	82	-
MC-5	822	-	123	52.5	202	1.25
low M oligomer	1200	0.08	88	24.5	235	-
oligomer	2200	0.30	-	-	390	1.31
low M polymer	3700	0.74	305^{xx}	-	430	1.38
polymer	-	1.41	313	9.0	441	1.40
polymer	-	3.10	316	15.5	>450	-
polymer	-	5.33	320	20.0	>450	-

x- calculated for the alkylphenylene terephthalate repeating unit xx- final peak temperature of the recrystallization-melting endotherm

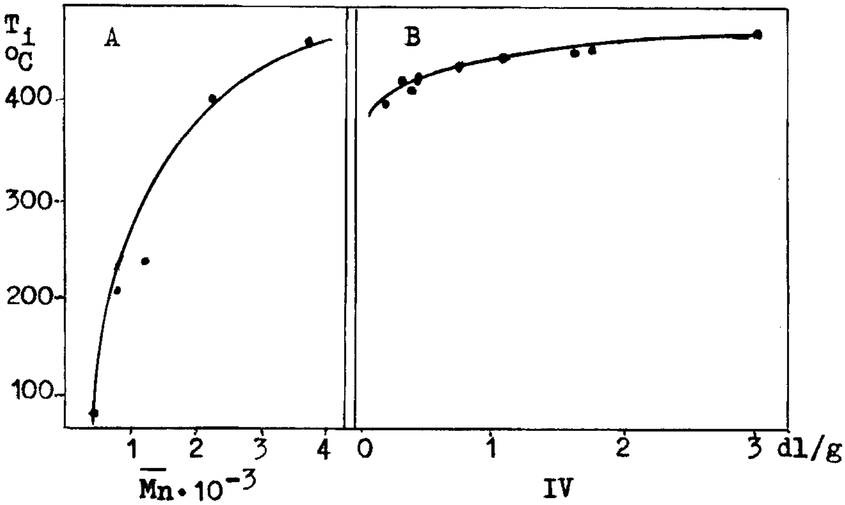


FIGURE 1. Molecular mass dependence of isotropisation temperature (T_i) for:
A- n-octyl substituted lower M samples
B- n-decyl substituted higher M samples

CONCLUSION

The alkyl group substitution on the aromatic rings in the rigid oligo- and polyesters allowed the study of LC behaviour of a wide range of samples from low to high M, in contrast to the unsubstituted ones.

The relationships between M and the properties of main chain rigid rod samples studied is slightly similar to that of oligo- and polymeric LCs containing flexible alkyl spacers. However, the formation of stable enantiotropic mesophases in alkyl substituted rigid rod oligomers occurs at lower M /~800/ when compared with those of containing flexible alkyl spacers /M~2200/[1]. The rigid lower M samples showed also a much stronger dependence of T_i on M than comparable LCs containing flexible alkyl spacers. Although at higher M the T_i is less dependent on M changes, it increases continously up to a polymer I.V. of 3 dl/g. As suggested by the isotropisation entropy values, it seems to exist an increasing order in the nematic phase with the increase of M.

The randomly distributed ASs along the main chain depressed not only the phase transition temperatures but also the crystallization ability, especially of low M polymers when compared to unsubstituted ones[3].

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