

Effects of monomer structure and copolymer composition on the glass transition temperature of binary liquid crystalline copoly(vinyl ether)s*

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The effects of monomer structure and copolymer composition on the glass transition temperature of binary liquid crystalline copoly(vinyl ether)s obtained via living cationic copolymerization of monomer pairs containing only mesogenic units and mesogenic and non-mesogenic units are discussed. The positive and negative deviations of the experimental glass transition temperatures from the calculated additive values were explained via the generation of an increased or decreased free volume in the copolymer. This dependence was qualitatively interpreted based on the structure of various monomer pairs.

(Keywords: liquid crystalline copoly(vinyl ether)s; glass transition temperature; free volume)

INTRODUCTION

Previous publications in this series reported on the influence of molecular weight and spacer length on the phase transitions of thermotropic poly(vinyl ether)s containing mesogenic side groups¹⁻⁸. Subsequently, the influence of copolymer composition on the phase behaviour of binary copoly(vinyl ether)s with homogeneous composition, constant molecular weight and narrow polydispersity was also investigated⁷⁻¹⁵. Both homopolymers and copolymers were synthesized by living cationic polymerization experiments¹⁻¹⁵. Although information on the influence of both molecular weight and copolymer composition on glass transition was available, we did not make any attempts to explain the latter⁷⁻¹⁵.

The goal of this paper is to discuss the influence of copolymer composition on the glass transition of liquid crystalline binary copolymers with constant molecular weight, well defined composition, and polydispersity of <1.15. The influence of the mesophase exhibited by the two homopolymers derived from the monomers used in the preparation of these binary copolymers on the glass transition temperature of copolymers will also be considered. Binary copolymers derived from

monomer pairs containing mesogenic units whose parent homopolymers exhibit: smectic A (S_A) and S_A , nematic (N) and N, S_A and N, S_A and glassy (G), chiral smectic C (S_C^*) and S_A , S_C^* and N, as well as binary copolymers derived from monomer pairs containing mesogenic and alkyl (butyl) side groups and whose parent homopolymers exhibit S_A and G will be discussed.

EXPERIMENTAL

The synthesis and characterization of the homopolymers and copolymers were presented in detail previously¹⁻¹⁵. All glass transition temperatures (T_g) were collected from the second heating scan at $20^\circ\text{C min}^{-1}$ on a Perkin-Elmer DSC-4 differential scanning calorimeter equipped with a TADS data station. Glass transition temperatures were read at the middle of the change in the heat capacity. A Carl-Zeiss optical polarized microscope (magnification $100\times$) equipped with a Mettler FP 82 hot stage and a Mettler FP 80 central processor was used to observe the thermal transitions and to verify the anisotropic textures. Relative molecular weights of polymers were measured with polystyrene standards by gel permeation chromatography (g.p.c.) by using a Perkin-Elmer Series 10 LC instrument equipped with LC-100 column oven and a Nelson Analytical 900 series integrator data station. A set of two Perkin-Elmer PL gel columns of 5×10^2 and 10^4 \AA with CHCl_3 as solvent (1 ml min^{-1}) were used. The measurements were made at 40°C using the ultraviolet detector.

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RESULTS AND DISCUSSION

Scheme 1 outlines the structure of all copolymers, the meaning of the short notation used in this paper, and the reference which describes their original synthesis and characterization. Table 1 summarizes the dependence of the glass transition temperature on copolymer composition and the range in which the number average molecular weight and the degree of polymerization of each series of copolymers varied. A capital letter was assigned to each copolymer in Table 1.

Figure 1 plots the dependence of the T_g on copolymer composition for copolymers. The dependence of the other phase transitions versus copolymer composition is available in the original publications⁹⁻¹⁵. The range in which the molecular weight of these copolymers varies is presented in Table 1. These copolymer systems can be classified into three distinct classes: (a) systems in which T_g values exhibit a negative deviation from their calculated additive values, i.e. poly[(6-11)-co-(6-2)]X/Y, poly[(6-11)-co-(6-3)]X/Y, poly[(6-11)-co-(6-5)]X/Y, poly[(6-11)-co-(6-6)]X/Y, poly[(6-8)-co-(6-2)]X/Y and poly[(15-8)-co-(6-3)]X/Y; (b) systems in which T_g values are almost equal to those of the calculated additive values, i.e. poly[(6-5)-co-(6-3)]X/Y, poly[(14-11)-co-(14-8)]X/Y and poly[(15-8)-co-(15-6)]X/Y; (c) systems in which T_g values exhibit a positive deviation from their calculated additive values, i.e. poly[(6-11)-co-(BVE)]X/Y.

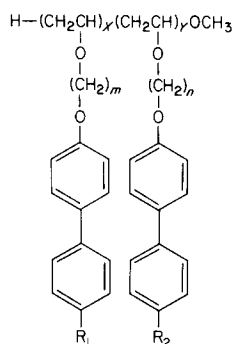
Systems of type a are specific for copolymers obtained from monomer pairs containing mesogenic groups

separated from their polymerizable group via flexible spacers of highly dissimilar length. Systems of type b are a subclass of type a in which the negative deviation of T_g is very small and, therefore, their T_g values can be considered about equal to that of the calculated additive value. These systems are obtained from monomer pairs containing mesogenic groups and flexible spacers of very similar length. Finally, systems of type c are obtained from monomer pairs containing a monomer with mesogenic side group which gives a homopolymer displaying a S_A mesophase, and a monomer containing a relatively short alkyl side group.

Attempts were made to fit the dependencies from Figure 1, starting with the flexible bond additivity equation elaborated by Gibbs and DiMarzio which accounts for the contribution to T_g of the fraction of flexible bonds in the copolymer¹⁶. The extended equations by Barton for diad¹⁷ and the equation of Ham for triad^{18,19} contributions to T_g were also tested.

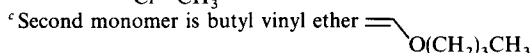
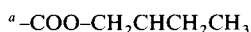
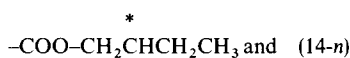
The experimental dependence of the T_g on composition of all copolymer systems of type a and b, which do not display large negative deviations of their T_g from the additive values, (i.e. deviations from the straight line connecting the end points) are fitted by the diad contribution equation¹⁷. The behaviour of copolymers poly[(6-11)-co-(6-2)]X/Y, poly[(6-11)-co-(6-3)]X/Y and poly[(15-8)-co-(6-3)]X/Y which display the largest negative deviations of their T_g , and poly[(6-11)-co-(BVE)]X/Y which exhibits positive deviations, was fitted only by the equation which includes the triad contributions¹⁸.

General structure of copolymers:



with m and $n=2$ to 11

R_1 and $R_2 = -CN$, (6-n)



Copolymers are labelled as follows:

Copolymer	Mesophase of each parent homopolymer		R_1	R_2	m	n	Ref.
	R_1	R_2					
Poly[(6-11)-co-(6-2)]X/Y	(s_A , g)	(s_A , g)	-CN	-CN	11	2	9
Poly[(6-11)-co-(6-3)]X/Y	(s_A , N)	(s_A , N)	-CN	-CN	11	3	12
Poly[(6-11)-co-(6-5)]X/Y	(s_A , s_A)	(s_A , s_A)	-CN	-CN	11	5	13
Poly[(6-11)-co-(6-6)]X/Y	(s_A , s_A)	(s_A , s_A)	-CN	-CN	11	6	12
Poly[(6-8)-co-(6-2)]X/Y	(s_A , g)	(s_A , g)	-CN	-CN	8	2	9, 10
Poly[(6-5)-co-(6-3)]X/Y	(s_A , N)	(s_A , N)	-CN	-CN	5	3	12
Poly[(14-11)-co-(14-8)]X/Y	(s_C^* , s_C^*)	(s_C^* , s_C^*)	MB ester ^a	MB ester	11	8	7
Poly[(15-8)-co-(15-6)]X/Y	(s_C^* , s_C^*)	(s_C^* , s_C^*)	CMP ester ^b	CMP ester	8	6	8
Poly[(15-8)-co-(6-3)]X/Y	(s_C^* , N)	(s_C^* , N)	CMP ester	-CN	8	3	15
Poly[(6-11)-co-(BVE)]X/Y	(s_A , g)	(s_A , g)	-CN	BVE ^c	11	BVE	14

Scheme 1 General structures of copolymers, the meaning of their short notation and the mesophase of each parent homopolymer

Table 1 Dependence of glass transition temperature (T_g) on copolymer composition

Copolymer composition X/Y (mol/mol)	T_g (°C) from second heating d.s.c. scan at 20°C min ⁻¹									
	A (6-11-co-6-2)	B (6-11-co-6-3)	C (6-11-co-6-5)	D (6-11-co-6-6)	E (6-8-co-6-2)	F (6-5-co-6-3)	G (14-11-co-14-8)	H (15-8-co-15-6)	I (15-8-co-6-3)	J (6-11-co-BVE)
0/10	78.3	60.0	28.5	29.1	72.8	60.0	8.0	16.7	60.0	-52.0 ^a
1/9	64.8	52.8	25.2	25.9	57.4	54.9	5.2	12.4	53.0	-27.8
2/8	55.8	44.2	20.4	18.9	48.3	50.8	6.1	11.5	41.3	-16.5
3/7	44.1	34.8	17.7	17.7	41.4	47.5	4.2	11.5	31.5	-11.4
4/6	35.8	27.7	15.3	15.4	36.0	44.5	3.3	11.2	26.3	-5.5
5/5	28.9	22.5	14.7	14.7	31.5	42.1	2.5	10.9	21.4	-0.25
6/4	20.0	17.5	15.7	17.5	21.3	38.8	3.2	10.4	18.2	2.5
7/3	15.0	15.6	13.5	11.0	18.2	34.2	3.7	11.1	14.8	5.7
8/2	14.8	14.0	12.7	10.8	16.3	31.4	3.3	11.1	14.1	9.5
9/1	13.3	14.1	12.5	12.1	14.3	27.7	6.6	11.6	14.1	12.1
10/0	12.5	14.0	14.0	14.0	11.6	28.5	8.2	15.0	16.1	14.0
$M_n \times 10^{-3}$ ^b	4.1-8.9	5.6-8.2	5.4-8.2	5.9-8.2	2.8-3.7	4.8-5.9	5.7-8.2	5.4-7.2	5.4-9.5	2.8-8.2
DP ^c	15-22	17-21	17-20	17-21	9-10	16-21	13-17	12-15	17-21	17-22

^a Ref. 20

^b Number average molecular weights were determined by g.p.c. using polystyrene standards as calibration plot and the polydispersities of all polymers are < 1.15

^c DP , degree of polymerization

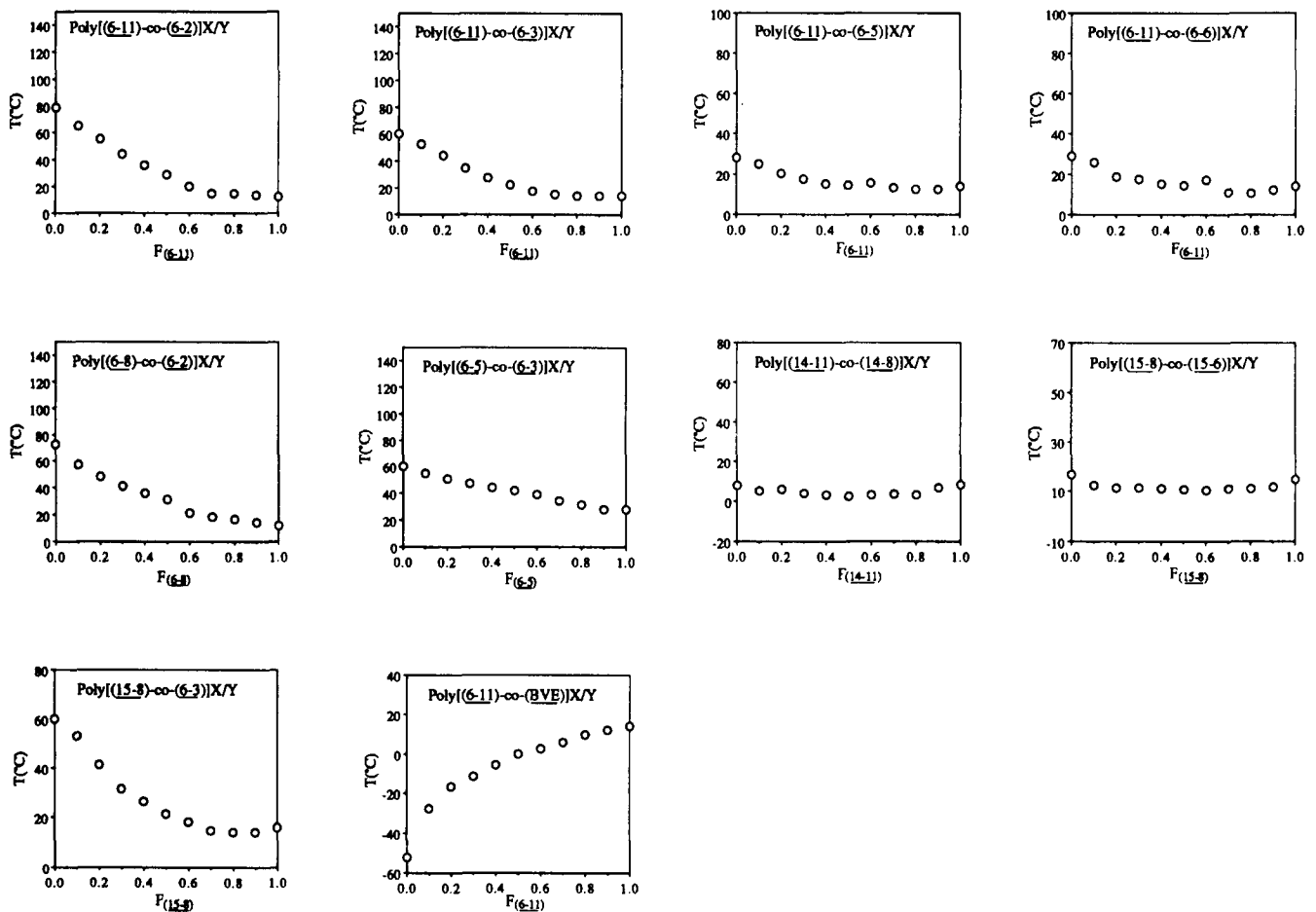


Figure 1 Glass transition temperature (T_g) of copolymers versus copolymer composition

Figure 2 displays the deviation of T_g from the additive value versus copolymer composition. The trend observed from this figure is similar to that in Figure 1 except that a quantitative comparison between all copolymer systems can be made. All copolymers derived from monomer

pairs containing mesogenic side groups show negative deviations of their T_g from the additive values. Only the copolymer based on the monomer pair containing mesogenic and aliphatic side groups shows a positive deviation of T_g from the additive value (Figure 2b).

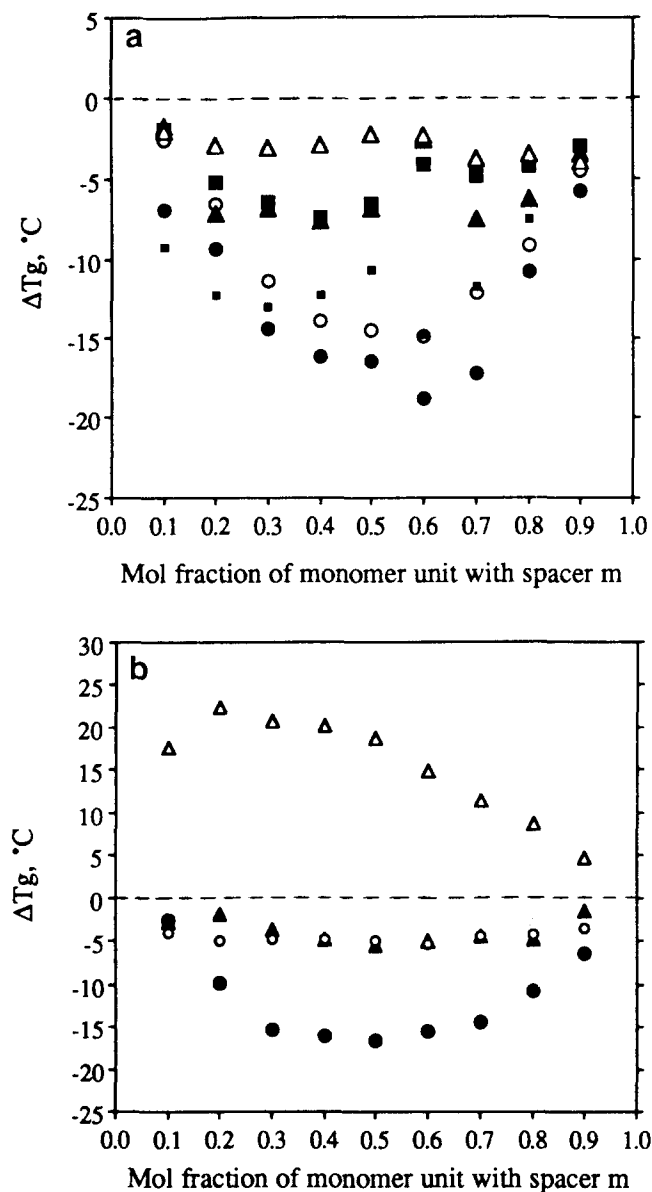
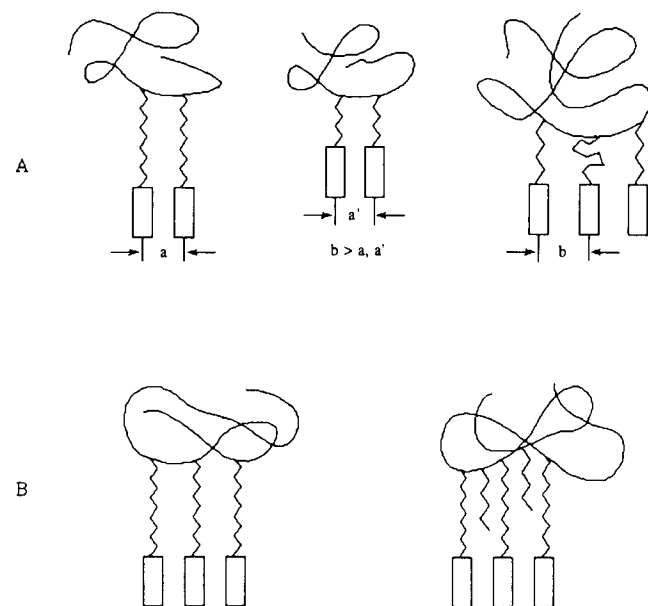


Figure 2 Dependence of the deviation of glass transition temperature (ΔT_g) versus copolymer composition: (a) ●, poly[(6-11)-co-(6-2)]; ○, poly[(6-11)-co-(6-3)]; ■, poly[(6-11)-co-(6-5)]; ▲, poly[(6-11)-co-(6-6)]; ▀, poly[(6-8)-co-(6-2)]; △, poly[(6-5)-co-(6-3)]; (b) ▲, poly[(14-11)-co-(14-8)]; ○, poly[(15-8)-co-(15-6)]; ●, poly[(15-8)-co-(6-3)]; △, poly[(6-11)-co-(BVE)]

The largest negative deviation of T_g (ΔT_g) is observed for copolymers generated from monomer pairs based on highly dissimilar spacer length. The large negative deviations of T_g from the additive values (Figure 2) are due to the creation of excess free volume upon copolymerization. The increase in the free volume induced by monomer pairs with highly dissimilar spacer length reaches the maximum around $X/Y=0.4-0.6$, leading to the minimum peak (i.e. maximum ΔT_g) in Figure 2a and b. By decreasing the difference between the length of the spacers of the monomer pair, the negative deviation of the T_g of the copolymers approaches the additive value. The generation of a liquid crystalline phase in the copolymers based on highly dissimilar spacer length and identical mesogenic groups creates a higher excess free volume than that in the homopolymers derived from the same two monomers. The formation in these copolymers of a smectic or nematic phase requires most

probably the contraction of the longest spacer. This contraction increases the width of the cross-section of the monomeric unit and, therefore, the free volume occupied by this monomeric unit increases (Scheme 2A).

Figure 3 plots the dependence of the negative deviation of T_g (ΔT_g) versus the ratio of the number of the methylenic groups in the flexible spacers of each monomer pair (m/n). The value of ΔT_g plotted in Figure 3 represents the average of the ΔT_g for the range 0.4–0.6 of the molar fraction of the monomeric unit with a spacer containing m methylenic groups (i.e. $X/Y=0.4-0.6$). The two plots in Figure 3 show that for each series of copolymers based



Scheme 2 Schematic representation of (A) the increased free volume generated in copolymers of type a and b and (B) the decreased free volume generated in copolymers of type c

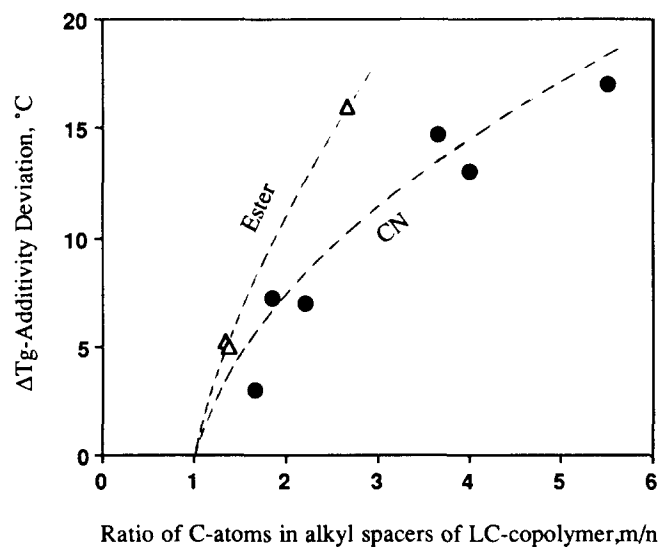


Figure 3 Dependence of the additivity deviation of T_g (ΔT_g) versus the ratio of the number of the methylenic groups in the flexible spacers of each monomer pair (m/n): △, ester {in the order poly[(15-8)-co-(15-6)], poly[(14-11)-co-(14-8)] and poly[(15-8)-co-(6-3)]}; ●, cyano {in the order poly[(6-5)-co-(6-3)], poly[(6-11)-co-(6-6)], poly[(6-11)-co-(6-5)], poly[(6-11)-co-(6-3)], poly[(6-8)-co-(6-2)] and poly[(6-11)-co-(6-2)]}

on an identical mesogenic unit, there is a direct correlation between ΔT_g and the m/n ratio. We can also observe that with the same m/n , ΔT_g of copolymers containing the bulkier ester tail group is higher than that of copolymers containing only the smaller -CN group. This is probably due to the closer packing in the glassy mesomorphic state of copolymers containing only the -CN group compared with copolymers containing the ester group. Therefore, ΔT_g is more affected in the former case.

The influence of the nature of the mesophase exhibited by the parent homopolymers on the ΔT_g deviation does not seem to be very significant (compare *Figures 1* and *2* and *Scheme 1*).

A positive deviation of T_g is observed only for the copolymer containing mesogenic and non-mesogenic units (*Figure 2*). This positive deviation is due to a decrease in the free volume upon copolymerization. The butyl group may act like a filler, which upon copolymerization fills in the free volume between the spacer groups of the structural unit containing mesogens better than in that of its parent liquid crystalline homopolymer (*Scheme 2B*). Therefore, the random copolymerization of a mesogenic monomer with a non-mesogenic monomer like BVE decreases the overall free volume of the copolymer *versus* that of its parent liquid crystalline homopolymer.

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