Anisotropic polymerization shrinkage behaviour of liquid-crystalline diacrylates

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Anisotropic polymerization shrinkage of liquid-crystalline acrylates has been studied. In order to investigate the changes occurring on the microscopic scale, X-ray diffraction was combined with density measurements. As a result it was shown that at high polymerization temperatures the polymerization shrinkage in the direction of the molecular orientation was higher than the shrinkage in the directions perpendicular to the molecular orientation. Subsequently the shrinkage obtained on the microscopic scale was compared with the results obtained on the macroscopic scale. The behaviour was interpreted in terms of the molecular structure and the packing density within the systems.

(Keywords: liquid crystals; acrylate; crosslinking; network; X-ray diffraction; packing density)

INTRODUCTION

The use of low-mass liquid-crystalline (LC) acrylates has recently been successfully demonstrated in the production of anisotropic networks[1–5]. These molecules possess low viscosities and they can be macroscopically oriented by a simple surface treatment, by flow or in electric and magnetic fields[6]. The induced orientation can subsequently be frozen in by isothermal photopolymerization[7] of the system. Highly crosslinked networks obtained in this way possess anisotropic thermal, mechanical, electrical and optical properties. In the present study we used a homologous series of liquid-crystalline diacrylates shown in *Figure 1* in order to investigate the anisotropic polymerization shrinkage that occurs in these systems. In order to study the shrinkage occurring on the microscopic scale, X-ray diffraction measurements were combined with density measurements. These results were then compared with the anisotropic linear shrinkage observed on the macroscopic scale.

EXPERIMENTAL

The structure of the monomers used for this study is given in *Figure 1*. Details of the syntheses and polymerization of the monomers can be found in refs. 2–4. The monomers were provided with 1% w/w of a photoinitiator, α,α-dimethoxydeoxybenzoin (Irgacure 651, Ciba Geigy). Polymerization of the materials was initiated by u.v. radiation from a 100 W high-pressure mercury lamp (366 nm, 10 mW cm^{-2}) in a nitrogen atmosphere. Densities in the liquid state were measured as a function of temperature from the mass and the length of samples in high-precision capillaries (0.5 mm in diameter) stored in an oven where the temperature was regulated (±0.1°C). Samples were polymerized in the liquid-crystalline state close to their isotropic transition temperature, and their densities at room temperature were measured using a density gradient column containing potassium carbonate in water. The thermal expansion behaviour of the solid samples was measured using a Perkin Elmer TMA7 unit. X-ray diffraction patterns were recorded by a Statton camera using Ni-filtered Cu K$_\alpha$ radiation. The camera was provided with a magnetic heating cell so that the temperature of the samples could be thermostatically controlled as the molecules were uniaxially oriented under the influence of the magnetic field (6 kG).

RESULTS AND DISCUSSION

Volume contraction during polymerization

In order to investigate volume changes occurring upon polymerization of LC acrylates, the densities of the materials were measured as a function of temperature before and after polymerization. In *Figure 2a* the densities of various monomers are plotted as a function of temperature. It can be seen that the density of the samples decreases with increasing number of methylene spacer groups. Density of a system is determined by the Van der Waals density ρ_W of the molecules as well as the empty volume within the system. One can represent the empty volume in terms of packing density K (ref. 8), which is defined as:

$$K = \frac{V_W}{M/\rho} = \frac{\rho}{\rho_W} \tag{1}$$

where ρ is the density, V_W is the Van der Waals volume occupied by the atoms of a molecule, M is the molecular weight and ρ_W is the Van der Waals density. In *Table 1* molecular weights of various samples are given together with their Van der Waals densities calculated according to Bondi[8]. Here it can be seen that the order obtained for the Van der Waals densities of the molecules is the same as the order found in *Figure 2a* at a given temperature. This indicates that at a given temperature

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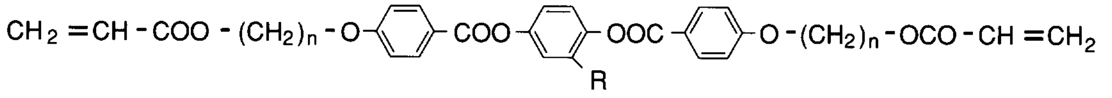

$$CH_2{=}CH{-}COO{-}(CH_2)_n{-}O{-}C_6H_4{-}COO{-}C_6H_3(R){-}OOC{-}C_6H_4{-}O{-}(CH_2)_n{-}OCO{-}CH{=}CH_2$$

C 4	n = 4	R = H
C 5	n = 5	R = H
C 6	n = 6	R = H
C 6 M	n = 6	$R = CH_3$
C 8	n = 8	R = H
C 10	n = 10	R = H

Figure 1 Molecular structure of the materials

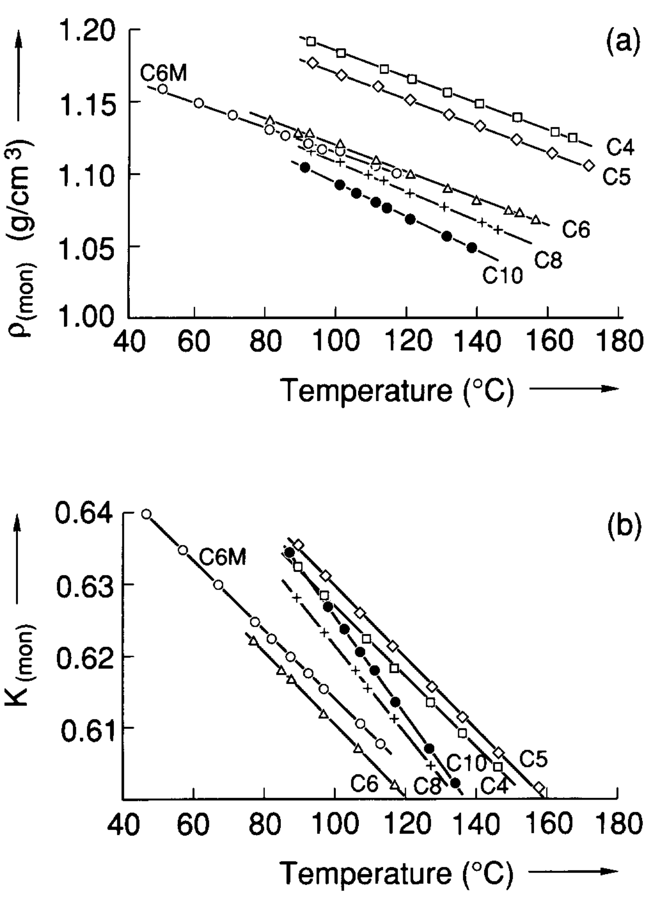

Figure 2 (a) Density and (b) packing density of the LC monomers as a function of temperature: (□) C4, (◇) C5, (△) C6, (+) C8, (●) C10, (○) C6M

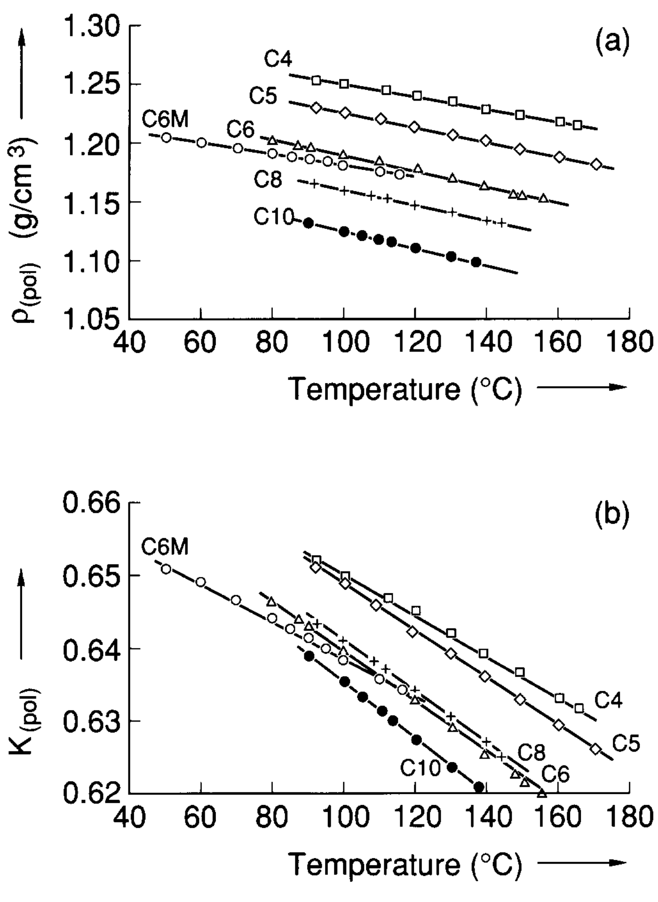

Figure 3 (a) Density and (b) packing density of the polymerized LC molecules as a function of temperature: (□) C4, (◇) C5, (△) C6, (+) C8, (●) C10, (○) C6M

packing densities of the molecules do not differ to a large extent. In *Figure 2b* packing densities of the molecules are plotted as a function of temperature. Here it can be seen that the order observed for the densities is no longer present and there is no correlation between the molecular length and the packing density of various molecules in the nematic state. It was expected that with increasing molecular length the intermolecular motions would also be reduced giving rise to improved packing. However intramolecular motions are influenced by the flexibility of the segments and steric hindrance within the system. It is probably because of a combination of these opposing effects that no order can be seen in the packing densities of various samples.

In *Figures 3a* and *3b* the densities and packing densities of polymerized samples are plotted. as a function of temperature. In all cases the degree of conversion of the double bonds as determined by infra-red measurements was above 95%. The density of the polymerized samples follows the same trend as the unpolymerized samples, showing higher density with decreasing number of methylene groups. When the packing densities of the polymerized samples are compared with those before polymerization, it can be seen that the relative positions of lines for various samples are changed, and except for C8 at a given temperature packing density within the polymerized samples increases with decreasing molecular length.

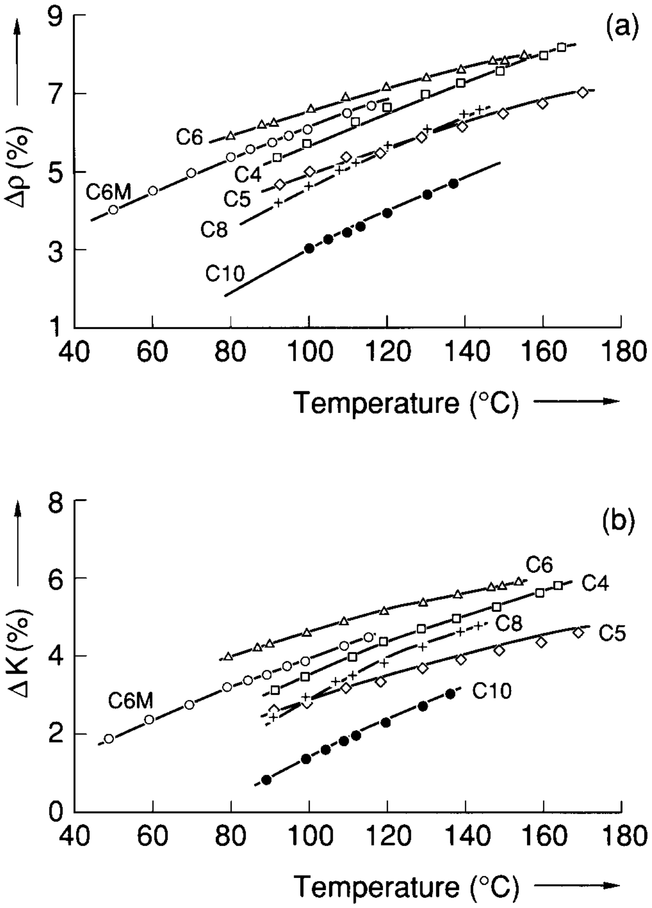

Figure 4 Difference in (a) density and (b) packing density of the liquid and polymerized systems: (□) C4, (◇) C5, (△) C6, (+) C8, (●) C10, (○) C6M

In *Figures 4a* and *4b* the polymerization shrinkage (change in density) and the change in packing density are plotted as a function of temperature. Here it can be seen that the shrinkage increases with increasing temperature and there is no correlation between the length of the molecules and the shrinkage. Volume contraction upon polymerization is generally considered[9,10] to be mainly due to (a) change in the Van der Waals volume of the molecules and (b) better packing of the molecules as a result of decreased entropy within the system. The change in the Van der Waals density ($\Delta\rho_W$) upon polymerization is given in *Table 1*. Here it can be seen that the change in the Van der Waals volumes which occurs as a result of opening the acrylate double bonds ($-CH{=}CH_2$) decreases with increasing molecular weight, i.e. decreasing acrylate concentration. It can also be seen that the shrinkage values shown in *Figure 4a* are higher than the values obtained in *Table 1*. Therefore the additional shrinkage observed in *Figure 4a* is caused by better packing of the molecules as a result of polymerization. The shrinkage caused by better packing can be influenced by the temperature and steric interactions. The effect of temperature can be seen in *Figure 4a* where for a given sample polymerization shrinkage increases with increasing temperature. This behaviour is associated with the empty volumes of the materials as a function of temperature in their liquid and solid states. It is well known that the mobility of the molecules is higher in the monomeric state than in the polymeric state. As a result the empty volume of the monomer increases more rapidly than that of the polymer with increasing temperature. Because of this, larger changes in the empty volume occur at higher polymerization temperatures. The effect of steric factors, which influence packing efficiency before and after polymerization, can be seen when C6 and C6M are compared. C6M has the same structure as C6 except for the methyl group substituted on the central aromatic ring. The methyl group in C6M reduces the mobility, giving rise to improved packing efficiency in the monomeric state (*Figure 2b*), and gives rise to a reduced packing efficiency in the polymeric state (*Figure 3b*) as compared with C6 owing to steric hindrance. Hence lower polymerization shrinkage is observed upon substitution of a methyl group on C6. Furthermore the change in the packing density upon polymerization was expected to be dependent on the formation of a number of crosslinks, which increase with increasing length of the monomer. However this is not observed and, as can be seen in *Figures 4a* and *4b*, the polymerization shrinkage only follows the trend observed for the change in their packing density. Therefore the absence of correlation between the molecular length and polymerization shrinkage probably also originates from steric effects.

Here it is interesting to point out that the polymerization shrinkage observed for the LC molecules under study is lower than that observed for epoxy–aromatic amine (8–9%)[9] and for acrylate networks (11–15%)[11]. This low shrinkage can be associated with high packing density of the LC monomers used here, 0.62–0.64 at 90°C, as compared with those for conventional diacrylates, 0.58–0.62[11]. If we take C10 as an extreme example, it shows a volume shrinkage of 2.3% at 90°C. Since 1.6% of this shrinkage is caused by reduction in the Van der Waals volume (*Table 1*), it means that only 0.7% of the shrinkage is caused by increased packing within the system upon polymerization.

Microscopic linear polymerization shrinkage

Having shown that the polymerization shrinkage in the LC samples is influenced to a large extent by the change in the packing density, we investigated polymerization shrinkage for various samples in various directions as a function of temperature. For this purpose X-ray diffraction was used. An example of an X-ray diffraction pattern obtained for an oriented sample in a magnetic field is shown in *Figure 5*. Bragg spacings (d_B) calculated for the equatorial peaks were taken as a measure of the intermolecular distance[12,13]. In *Figure 6*, d_B is plotted as a function of temperature. Here it can be seen that there is no correlation between d_B and the length of the monomer (number of methylene groups). Since the packing within the systems does not necessarily need to be the same, it is not appropriate to compare the d_B obtained for various samples. However, the slopes of the lines can be used to compare expansion coefficients

Table 1 Various properties of the monomer and the polymer

Sample	*M* (g mol^{-1})	ρ_W (mon) (g cm^{-3})	ρ_W (pol) (g cm^{-3})	$\Delta\rho_W$ (%)
C4	602	1.884	1.925	2.15
C5	636	1.853	1.89	2.02
C6	658	1.825	1.86	1.96
C6M	672	1.811	1.85	1.90
C8	714	1.78	1.81	1.71
C10	770	1.742	1.77	1.55

of the samples in the direction perpendicular to molecular orientation ($\alpha_\perp$), assuming cylindrical symmetry within the systems where the packing remains the same with increasing temperature. Furthermore, the expansion coefficient of the samples in the direction of molecular orientation ($\alpha_\parallel$) was estimated from the volume expansion coefficient (α_v) assuming $\alpha_v = 2\alpha_\perp + \alpha_\parallel$. In *Table 2* volume expansion coefficients for the monomers and the polymers and the expansion coefficients in various directions for the monomers are given together with the glass transition (T_g) temperatures[5] for the polymers. Here it can be seen that the volume expansion coefficients of both the monomers in the nematic state and the polymers in the rubbery state increase with increasing number of methylene groups, indicating that the increasing number of flexible units within the system causes the increase in mobility. It can also be seen that there is a net contraction in the direction of molecular orientation, and except for C5 the coefficient of expansion in the direction perpendicular to the molecular orientation exceeds the volume expansion coefficient. This behaviour is also observed for polymerized samples using t.m.a. In *Figure 7* the expansion behaviour of a macroscopically oriented sample in the direction parallel ($\alpha_\parallel = -1.5 \times 10^{-4}\,°C^{-1}$) and perpendicular ($\alpha_\perp = 3.8 \times 10^{-4}\,°C^{-1}$) to the molecular orientation is plotted together with the calculated average linear expansion and the measured linear expansion for an isotropic sample. As can be seen there is a net contraction in the direction of molecular orientation whereas the expansion in the direction perpendicular to the molecular orientation exceeds the isotropic linear expansion. The expansion coefficients obtained in the monomeric state in the two major directions exceed the values obtained for the polymer. This again indicates that upon polymerization the mobility is reduced to a large extent within the systems.

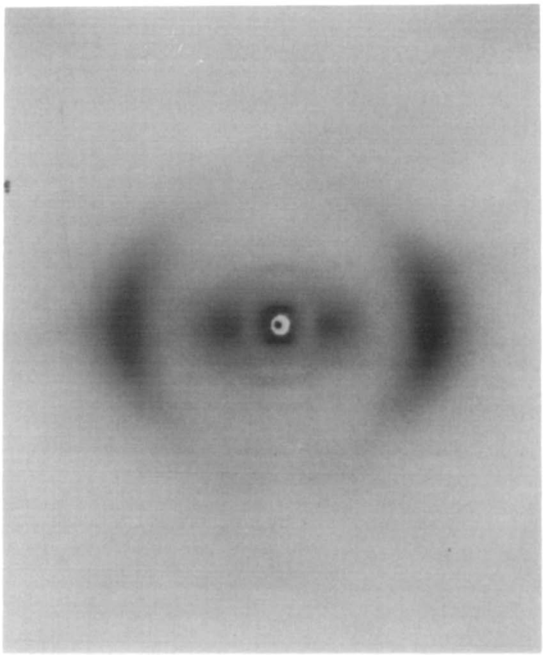

Figure 5 X-ray diffraction photograph of an oriented sample. Direction of molecular orientation is vertical

We tried to correlate this behaviour of the molecules in the monomeric state with the loss of order within the nematic system. In *Figure 8* we show two rod-like units, which have length x and their ends are y apart. As the rods make an angle θ due to the loss of order and y increases due to thermal motion, the net change of distance between the centres of the molecules in the

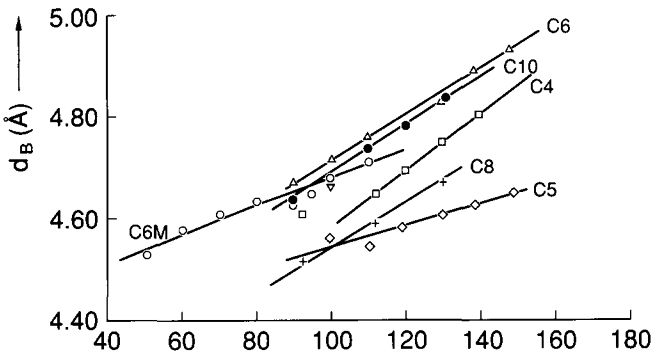

Figure 6 Bragg spacing d_B for various monomers as a function of temperature: (□) C4, (◇) C5, (△) C6, (+) C8, (●) C10, (○) C6M

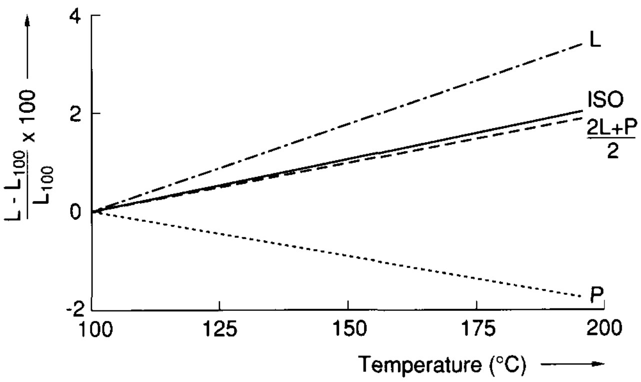

Figure 7 Expansion of polymerized C6 in the directions P = parallel and L = perpendicular to the molecular orientation; Iso = linear expansion of an isotropic sample

Table 2 Expansion coefficients of various samples together with their glass transition temperatures in the polymeric state

Sample	T_g (°C)	α_v (mon) (°C^{-1})	α_v (pol) (°C^{-1})	$\alpha_\perp$ (mon) (°C^{-1})	$\alpha_\parallel$ (mon) (°C^{-1})
C4	118	7.8×10^{-4}	4.5×10^{-4}	12.1×10^{-4}	-16.4×10^{-4}
C5	110	7.9×10^{-4}	5.4×10^{-4}	4.3×10^{-4}	-6.2×10^{-5}
C6	83	8.1×10^{-4}	6.1×10^{-4}	9.0×10^{-4}	-9.9×10^{-4}
C6M	83	7.6×10^{-4}	5.2×10^{-4}	5.6×10^{-4}	-3.6×10^{-4}
C8	71	9.8×10^{-4}	6.2×10^{-4}	8.8×10^{-4}	-7.4×10^{-4}
C10	55	10.5×10^{-4}	6.3×10^{-4}	8.8×10^{-4}	-6.7×10^{-4}

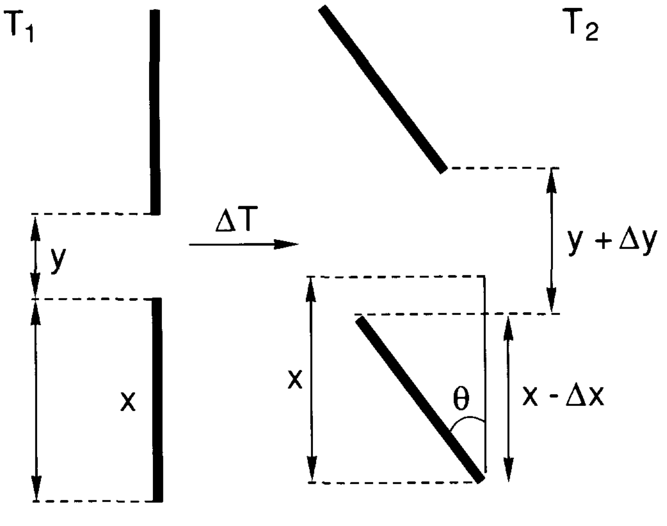

Figure 8 Schematic representation of rod-like units at two temperatures $T_1 < T_2$

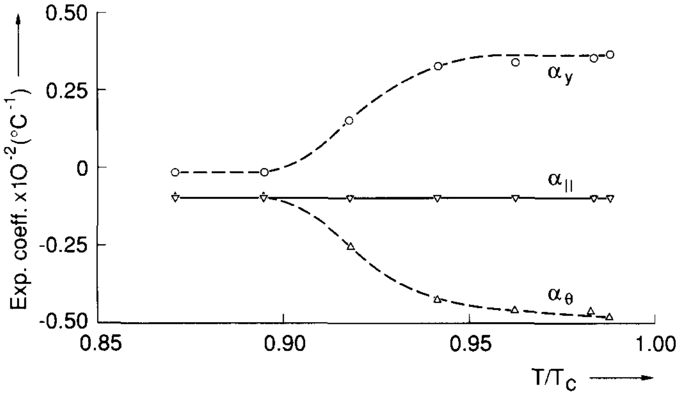

Figure 9 Expansion coefficients in the direction of molecular orientation as a function of temperature

direction of molecular orientation can be written as:

$$\Delta l = \Delta x + \Delta y = \Delta y - (1 - \cos\theta)x \qquad (2)$$

Assuming that $y \ll x$ and $\Delta l = \Delta T(x + y)\alpha_{\|}$ equation (2) can be rewritten as:

$$\alpha_{\|} = \frac{1 - \cos\theta}{\Delta T} + \frac{\Delta y}{\Delta T x} = \alpha_\theta + \alpha_y \qquad (3)$$

In *Figure 9* we assumed an idealized case and used values obtained from ref. 4 for the order parameter defined as $S = \langle \frac{3}{2}\cos^2\theta - \frac{1}{2} \rangle$ for C6 to plot the coefficient of contraction α_θ due to the loss of order and the calculated values of expansion coefficient α_y between the ends of the molecules as a function of the reduced temperature. Here it can be seen that decrease of order can account for the contraction in the direction of molecular orientation.

In order to calculate anisotropic polymerization shrinkage, X-ray diffraction patterns were also obtained before and after polymerization, and the change in d_B was used to calculate the polymerization shrinkage in the direction perpendicular to the molecular orientation $s_\perp$ at various temperatures. Subsequently volume shrinkage s_v was used to calculate the shrinkage in the direction of molecular orientation $s_{\|}$ assuming $s_v = 2s_\perp + s_{\|}$. In *Figure 10* polymerization shrinkage in the directions perpendicular and parallel to the molecular orientation is shown. Here it can be seen that $s_\perp$ tends to increase with increasing temperature, where $s_{\|}$ tends to decrease. The decrease in the polymerization shrinkage in the direction of molecular orientation can be associated with an increase in the order that occurs during polymerization at high temperatures. Increase of order during polymerization results in an expansion in the direction of molecular orientation compensating partly for the shrinkage. Indeed the effect of an increase in order upon polymerization has already been observed[3]. Furthermore in *Figure 10* it can be seen that for almost all of the samples (except for C8 and C10 at high temperatures) $s_{\|}$ is always greater than $s_\perp$. This can be associated with the packing of the molecules in the direction perpendicular to molecular orientation. If we assume a random arrangement of the molecules, then the nearest-neighbour distance d_n can be calculated as[12] $d_n = 1.117 d_B$, giving values in the range of 4.9–5.1 Å for various samples at various temperatures. Since the width of the phenyl ring is about 6.4 Å, free rotation of the molecules is greatly hindered[13], indicating high packing of the central aromatic unit of the molecules. Therefore it is probably the high packing of the central units that gives rise to low polymerization shrinkage.

Macroscopic linear shrinkage

Having shown that upon polymerization the LC molecules on microscopic scale give rise to anisotropic

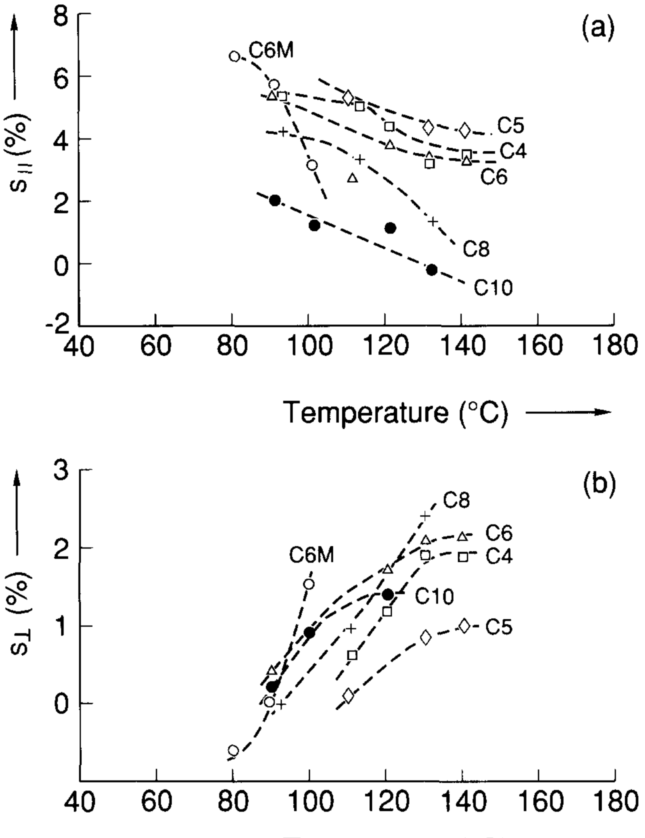

Figure 10 Microscopic polymerization shrinkage as a function of polymerization temperature for various molecules (a) in the direction parallel to molecular orientation and (b) in the direction perpendicular to molecular orientation: (□) C4, (◇) C5, (△) C6, (+) C8, (●) C10, (○) C6M

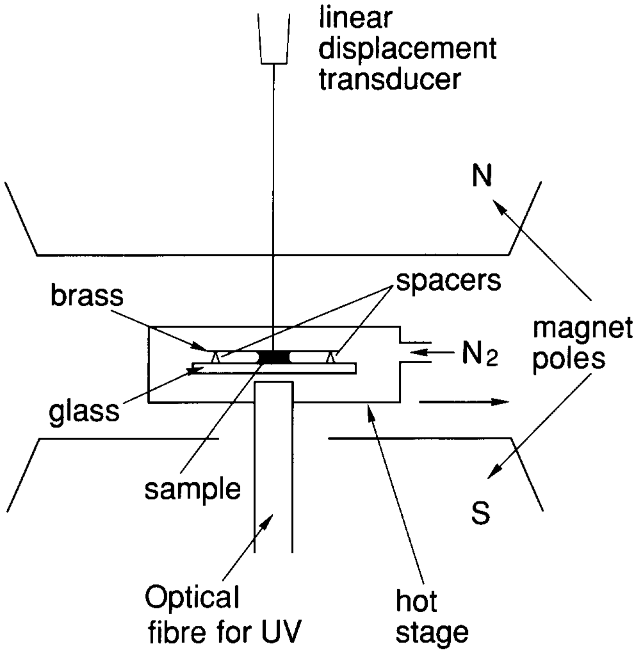

Figure 11 Schematic drawing of the set-up used for measuring macroscopic shrinkage

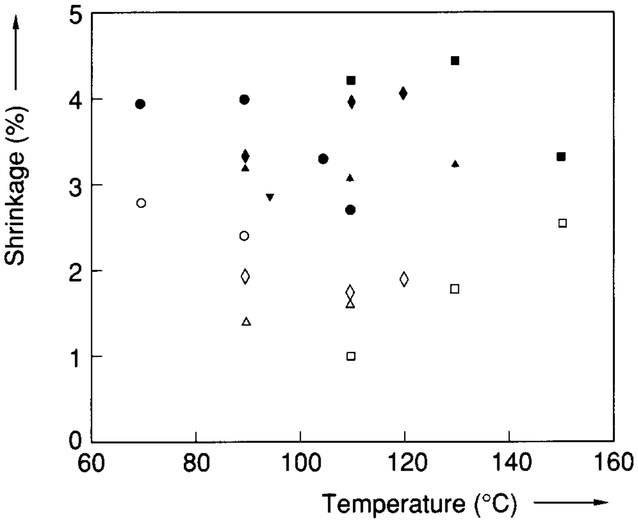

Figure 12 Macroscopic polymerization shrinkage as a function of polymerization temperature for various molecules: open symbols = in the direction perpendicular to molecular orientation; closed symbols = in the direction of molecular orientation: (□) C4, (◇) C5, (△) C6, (▽) C10, (○) C6M

Table 3 Room-temperature densities of various samples

Sample	ρ (mon) ($g\,cm^{-3}$)	K (mon)	ρ (pol) ($g\,cm^{-3}$)	K (pol)	$\Delta\rho$ (%)
C4	1.300	0.690	1.280	0.665	−1.5
C5	1.255	0.677	1.260	0.666	0.4
C6	1.243	0.681	1.229	0.661	−1.1
C6M	1.212	0.669	1.215	0.657	0.2
C8	1.184	0.680	1.202	0.664	1.5
C10	1.177	0.675	1.172	0.662	−0.04

polymerization shrinkage, we tried to measure the linear anisotropic shrinkage on the macroscopic scale using oriented samples. The set-up used for this purpose is shown in *Figure 11*. The materials (5 mg) were held between a thick glass plate and a 200 μm thick 5 mm wide copper plate, which were separated by two 1 mm thick spacers set 1 cm apart. The sample temperature was thermostatically controlled in a hot stage. A linear displacement transducer placed on top of the copper plate was used to measure the displacement caused by polymerization shrinkage. The alignment of the molecules perpendicular and parallel to the substrates was achieved in a magnet and using rubbed polyimide layers. Polymerization was carried out using a mercury light source supplied with a waveguide. In *Figure 12* shrinkage for various samples is plotted as a function of temperature in the two major directions. Here it can be seen that the measured shrinkage is anisotropic and is in good agreement with the results obtained on the microscopic scale. However, here it is important to point out that the linear shrinkage is always difficult to measure and contributions from the bulk are always obtained. Here we tried to take the length-to-diameter ratio of the material to be as large as possible to reduce the volume contributions to the shrinkage as much as possible. Nevertheless, volume contributions to the shrinkage were present, as the linear shrinkage measured for an isotropic diacrylate using the aforesaid set-up was about 20% more than the actual linear shrinkage estimated from density measurements.

Room-temperature densities

Having investigated the shrinkage behaviour of LC materials at high temperatures, we compared the densities of LC monomers in the crystalline state with those of the crosslinked polymers at room temperature. In *Table 3* room-temperature densities and packing densities of various samples are given. Here it can be seen that the densities of the samples in both the monomeric and the polymeric states decrease with increasing molecular weight. Furthermore it can also be seen that the densities of C8, C6M and C5 in the polymeric state are higher than the densities of the materials in their monomeric crystalline states, whereas the others show the opposite behaviour. However, when the packing densities of the materials are compared, it can be seen that the packing densities in the monomeric state are higher than in the polymeric state. This indicates that upon polymerization, even though in all cases a decrease in the Van der Waals volume of the molecules occurred, this decrease in the case of C4, C6 and C10 was less than the increase in the empty volume.

CONCLUSIONS

Polymerization-induced shrinkage in LC acrylate systems was studied. It has been shown that LC acrylates in the oriented state show anisotropic polymerization shrinkage. Densities of the materials in both the polymeric and the monomeric states were found to be influenced by the Van der Waals densities rather than the empty volume within the systems. The volume shrinkage upon polymerization was found to be greater than Van der Waals volume changes and the extra shrinkage was associated with the improved packing density upon polymerization. The change in the packing density was found to be influenced by the temperature and the steric hindrance. The polymerization shrinkage in the LC acrylate systems was found to be lower than the shrinkage commonly observed for conventional acrylates. Low shrinkage behaviour of the LC acrylates was associated with the initially high packing density within the systems. X-ray diffraction measurements showed that polymerization shrinkage on the microscopic scale was anisotropic and in most cases the shrinkage in the direction of molecular orientation was found to be greater than in lateral directions. The trend observed for the microscopic anisotropic shrinkage behaviour was also found on the macroscopic scale despite volume contributions to the linear shrinkage measurements. Finally when room-temperature densities of the polymers and the monomers were compared, it was found that some of the materials showed higher densities in the polymeric state than in the crystalline monomeric state.

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