Physical ageing in a thermotropic liquid-crystalline polymer

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The effects of physical ageing on the mechanical properties of a liquid-crystalline copolyester (LCP) were determined. Creep measurements in torsion as a function of ageing time were performed on macroscopically unoriented samples in the temperature range of −60 to 180°C. Below the glass transition temperature ($T_g \simeq 100$°C), the results indicate physical ageing effects analogous to those of flexible polymers. However, the curvature exponent of the compliance as a function of creep time of the LCP is distinctly smaller. Above T_g, physical ageing remains present while additional annealing effects arise. The molecular interpretation of the time dependence of mechanical properties in LCPs cannot rely upon free-volume concepts as in flexible polymers, but might be based on new structural models that were recently introduced.

(Keywords: liquid-crystalline polymer; physical ageing; mechanical properties)

INTRODUCTION

Physical ageing is a well known phenomenon affecting the time-dependent properties of amorphous and semicrystalline flexible polymers[1,2]. Since physical ageing implies a decrease in molecular mobility, the process most prominently manifests itself in properties like the viscoelastic mechanical behaviour, dielectric relaxation and gas permeability. Mechanical creep measurements are often employed for a determination of the influence of physical ageing on relaxation processes. In a certain temperature range below T_g, short-term creep curves almost uniformly shift to longer creep times (on a logarithmic scale) under the action of physical ageing, thus reflecting the ever-increasing relaxation times. Below the temperature of the first secondary transition (T_β), the rate of ageing reduces substantially owing to the strong decrease in molecular mobility. In amorphous polymers, the upper limit of the ageing range is set by the glass transition temperature; whereas in semicrystalline polymers, the influence of the process extends well into the rubbery phase. This is explained by the extended glass transition model, in which the molecular mobility (which is in fact exceedingly high in the amorphous parts of the rubbery phase) is supposed to be restricted in the amorphous–crystalline transition regions[2]. Moreover, in the range between T_g and the melting temperature, crystallization interferes with physical ageing and, on a molecular level, the two processes might even be indistinguishable.

In the solid state, thermotropic main-chain liquid-crystalline polymers (LCPs) behave similarly to semicrystalline flexible polymers in many respects. The main difference is the structural arrangement on a molecular level, i.e. the presence of oriented microscopic domains in the case of LCPs. Consequently the rearrangement process on the molecular scale is expected to be distinct as well. In (commercially available) thermotropic copolyesters, the polymers of interest in the present investigation, the random sequence distribution imposes an extra parameter for the molecular reordering process. So, although physical ageing may be anticipated in LCPs because of their partly amorphous character, the actual mechanism and the effect on macroscopic properties might be quite different from that in (semi-)flexible polymers. In this respect two features might be indicative, namely the possibly dissimilar nature of the glass transition and the observed absence of detectable density differences between the crystalline and amorphous phases in some LCPs. Especially this second point is of great interest in the present investigation, since the phenomenon of physical ageing is often explained in terms of relaxation of the free volume[1] of the amorphous fraction. In the following the two points will be considered in more detail.

Glass transition

In the widely investigated series of thermotropic main-chain random copolyesters, a glass transition is generally identified around 100°C by d.s.c. as well as dynamic measurements. Cao and Wunderlich[3] studied the exceptional width of the T_g transition in a specific range of compositions. Although a certain broadening of the transition is observed frequently in LCPs, this does not provide direct evidence about its nature. Wendorff and coworkers[4,5] determined the increase in heat capacity at T_g as a function of the crystallinity (induced by annealing at temperatures between T_g and the transition to the nematic melt, T_m). Since no specific dependence upon the degree of crystallinity was observed, they concluded that the transition takes place equally in the crystalline phase. This rather controversial idea was partly supported by their studies of the crystallization rate as a function of temperature. Unlike the situation

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in flexible polymers, where the crystallization rate drastically decreases on approaching T_g from above and equals zero below T_g, they observed a gradually decreasing rate, reaching a finite value below T_g. This would imply sufficient residual motion in the glassy state to enable the crystallization to continue. On the other hand, residual motion also accounts for the physical ageing process. However, it is difficult to conceive two distinct reordering mechanisms on the molecular level, one leading to an enthalpy increase at T_m, the other at T_g. Combined with the idea that the glass transition also occurs in the crystalline part, this would mean a strongly modified view of semicrystallinity in such systems. Obviously this subject awaits further investigation. The enthalpic relaxation due to physical ageing, as manifested by the development of a peak in the d.s.c. trace at T_g, has been reported in main-chain LCPs by several authors[6–10]. These observations are very similar to those in flexible polymers and indicate that at least in some properties the (random) copolyesters exhibit common effects as the result of physical ageing.

Volume effects

In flexible polymers, the melting transition is accompanied by an increase in specific volume of the order of 1–10%. In main-chain thermotropic copolyesters, however, there is evidence for zero or non-detectable volume changes at the solid–nematic transition[11] (note that the melting enthalpy in this case is only about 10% of the amount in flexible semicrystalline polymers). Moreover, no dependence of the density upon the degree of crystallinity was found. These observations imply a negligible density difference between the amorphous and crystalline fractions. It is unclear whether this is a general characteristic of this class of LCPs. Hsiao *et al.*[12] observed a very small volume change ($\simeq$0.5%) upon melting in another LC copolyester, while the data of Walsh *et al.*[13] reveal no transition-induced volume changes in a comparable system. The latter authors also included measurements on a range of main-chain homopolymers exhibiting normal volume changes ($\simeq$4%) upon melting. Finally, in LC side-chain polymers, small but distinct volume changes occur at melting[14]. The overall conclusion may be that in main-chain random copolyesters the volume change at the solid–nematic transition is vanishingly small or at least an order of magnitude smaller than in flexible semicrystalline polymers. This conclusion does not apply to main-chain homopolymers or LC side-chain polymers. Since the crystalline packing is considered to have the highest density, it is anticipated that the volume relaxation as a consequence of physical ageing in the LC copolyesters is also of another magnitude than observed in flexible polymers. Indeed, two studies on (commercial) random copolyesters[6,8] reveal no observable volume effect upon prolonged ageing just below T_g. This means that actual volume changes are much smaller than the experimental error of at most 0.1%. Since flexible polymers exhibit a volume relaxation of 0.1–1% at advanced ageing times, we can state that in the random copolymers the physical ageing is accompanied by volume effects that are also at least an order of magnitude smaller (and hardly detectable). If volume relaxation is the driving force behind physical ageing, as assumed in free-volume models, this would have its consequence on the observed effects in time-dependent properties.

The above remarks on the T_g characteristics and volume effects in LC random copolyesters make clear that the understanding of ordering phenomena in these systems is still far from complete. The exact mechanism of the various transitions on a microscopic scale and the differences with systems exhibiting other types of LC behaviour remain unclear. Moreover, there is still much uncertainty about the role of randomness in time-dependent phenomena of (commercial) copolyesters, especially with regard to (re-)crystallization processes[3,4,15–17]. The aim of the present investigation is to get more experimental information on time-dependent behaviour in a wide temperature range around T_g. We will focus on a description in terms of physical ageing in combination with (re-)crystallization, since this allows the most direct comparison with flexible polymers[2]. The property of interest will be the time-dependent creep compliance because of its sensitivity to molecular relaxation rates. Creep measurements on LCPs with this intent have not been reported before. There was some initial research on time dependence of creep behaviour in rigid-chain polymers (non-LC)[18], indicating a less-pronounced shifting effect with ageing. Such a slow-down in comparison with physical ageing in flexible polymers was also inferred from enthalpy relaxations in a random LC copolyester[8]. However, the evidence is far from conclusive. Apart from the fundamental interest, the present, more detailed, investigation of the time- and temperature-dependent creep properties in a commercial thermotropic LCP may also yield valuable information on the long-term mechanical behaviour, using extrapolation methods according to Struik[1].

EXPERIMENTAL

The LCP selected for the experiments is Vectra A900 (trademark of Hoechst Celanese Corp.), an aromatic random copolyester consisting of 73% *p*-hydroxybenzoic acid (HBA) and 27% 2-hydroxy-6-naphthoic acid (HNA). The melting transition to the liquid-crystalline state is located at 280°C. The glass transition is observed at about 100°C, while the more frequency-dependent β-transition takes place around room temperature (peak temperature about 20°C at 1 Hz)[19]. Test samples were made by grinding granules under cyrogenic circumstances followed by compression moulding into plaques at 300°C for several minutes. The plaques were quenched to room temperature and bars with approximate dimensions $7 \times 3 \times 150\,\mathrm{mm}^3$ were cut from them. In this way reproducible test specimens could be obtained of macroscopically unoriented material with an estimated crystallinity[20] around 20%.

Creep measurements in torsion were performed on an apparatus as described by Struik[1]. The rectangular test bars were loaded to a strain of at most 0.3%. In order to probe ageing effects, the time dependence of the creep compliance in torsion was determined by successive isothermal short-term creep tests. In a short-term creep experiment, illustrated in *Figure 1*, the creep time t is short with respect to the ageing time t_e, so that ageing effects are negligible during an individual creep test. Comparison of creep curves recorded at different ageing times gives direct information on the relaxation rates involved. The complete lay-out of a short-term creep experiment is as follows. First, previous ageing effects have to be erased by temporarily heating the sample to

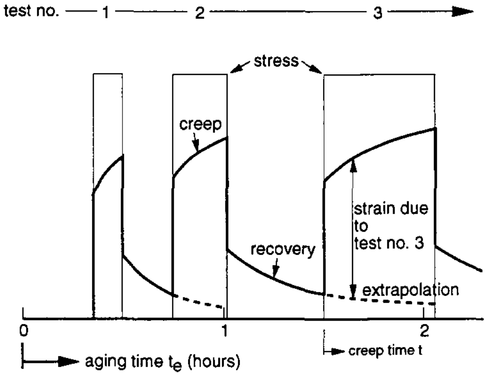

Figure 1 Lay-out of a series of isothermal short-term creep measurements

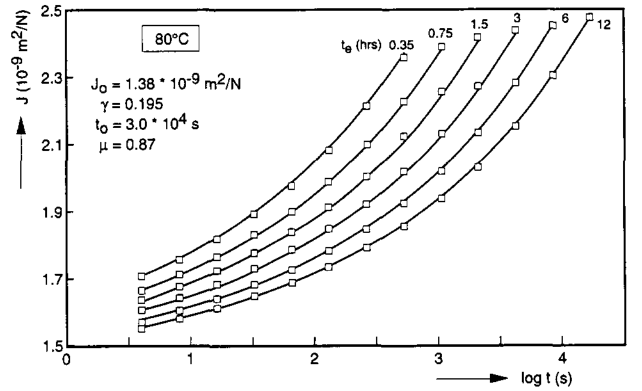

Figure 2 Results of short-term creep experiments in torsion at 80°C. Full curves represent best-fit curves on the basis of the indicated parameter values

a temperature at which the regions responsible for the ageing have gained complete mobility. For measuring temperatures below T_g (ageing in the fully amorphous regions), this rejuvenation can be achieved just above T_g; whereas for measuring temperatures above T_g (ageing in the amorphous–crystalline transition regions), some distinctly higher temperature has to be selected. Then the sample is quenched to 40°C below the measuring temperature, the clamps are tightened and the measuring temperature is set. At this moment actual ageing commences. After an elapsed time of 21 min, in which the sample temperature settles, the first creep test is started (duration about 8.5 min). At regularly increasing ageing times, subsequent creep tests are run, up to a maximum ageing of 12 h (followed by a test duration of about 4.5 h). In between two successive creep tests the recovery strain is recorded and an extrapolation of these data is used for correction of the creep strain. Several samples were included in the research programme.

RESULTS

Series of isothermal short-term creep measurements were carried out in the temperature range of −60 up to 180°C. In the experiments below T_g, performed at intervals of 20°C, the rejuvenation took place at 140°C for 30 min. This pretreatment can be considered as a real erasure of previous physical ageing effects, as became evident from the reproducibility of results ascertained in various tests. In *Figure 2* the experimental data for a measurement at 80°C are depicted, namely torsional creep compliance J *versus* the logarithm of creep time t at six different ageing times t_e. The full curves in this figure represent the results of non-linear least-squares curve fitting (Levenberg–Marquardt algorithm) using the Kohlrausch–Williams–Watts (KWW) relation[1] for the time dependence of the short-term creep compliance:

$$J(t)=J_0\exp\left(\frac{t}{t_0}\right)^{\gamma} \qquad (1)$$

In this relation t_0 sets a reference for the relaxation time while γ describes the curvature. The fitting was based on the assumption of uniform horizontal shifts of the entire creep curves on a logarithmic time scale. This implies the incorporation of only one adjustable value of J_0, the curvature exponent γ and the horizontal shift rate μ, the latter being related to the horizontal shift $\log a$ by:

$$\mu=-\frac{\mathrm{d}\log a}{\mathrm{d}\log t_e} \qquad (2)$$

Note that the relation between the horizontal shift and the reference relaxation time is expressed as:

$$a(t_{e2},t_{e1})=\frac{t_0(t_{e1})}{t_0(t_{e2})}=\left(\frac{t_{e1}}{t_{e2}}\right)^{\mu} \qquad (3)$$

The final parameter values (inaccuracies of a few per cent) are indicated in the figure, where t_0 refers to an ageing time of 1 h. As can be seen, the simultaneous fitting yields excellent results, thereby showing that the common ageing concept involving simple shift behaviour of short-term creep equally applies to this random LC copolymer. The value of the horizontal shift rate (accuracy ±0.02) compares very well to that of flexible polymers. However, the curvature exponent of the creep compliance turns out to be distinctly smaller than generally encountered in flexible polymers ($\gamma = 0.30$–0.35), which might in itself be indicative of some inherent differences in reordering phenomena on a molecular level.

Further examples of isothermal short-term creep series below T_g are presented in *Figures 3* and *4* for temperatures of 20 and −40°C respectively. The experimental data at 20°C and low creep times clearly display features of passing the secondary transition. Therefore the fitting at this temperature has been performed at higher creep times only, resulting in normal shifting behaviour. Effects of passing the secondary transition were also observed at 40 and 0°C, and led to larger inaccuracies in final parameter values. At −40°C, appreciably below the secondary transition, full agreement between experimental data and simultaneously fitted curves is

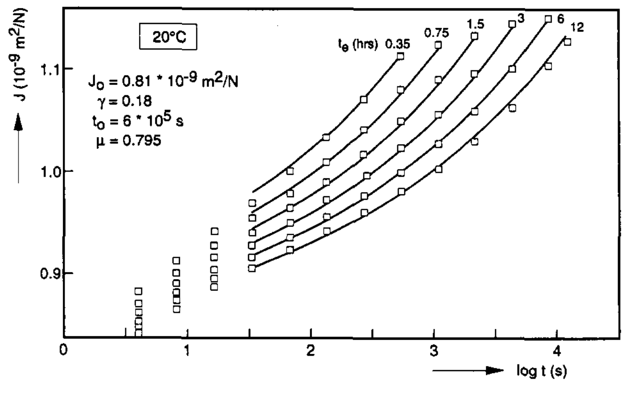

Figure 3 Experimental data and best-fit curves (high creep times only) at 20°C

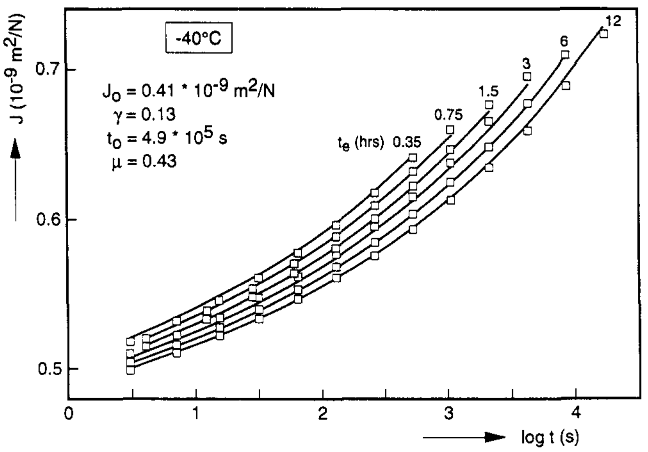

Figure 4 Experimental data and best-fit curves at −40°C

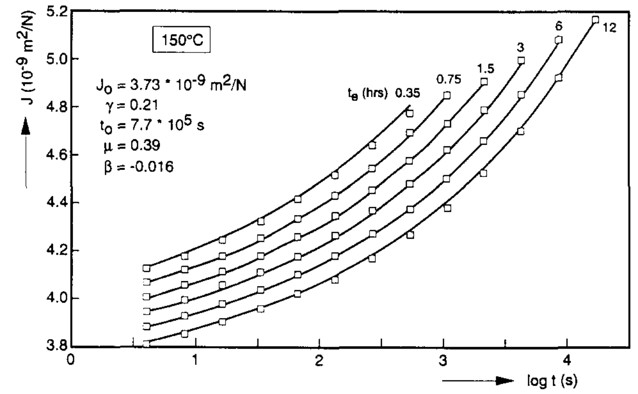

Figure 5 Experimental data and best-fit curves at 150°C

again present. The shifting rate, however, has decreased substantially, thereby manifesting the gradual vanishing of physical ageing effects at these low temperatures. Results at −60°C ($\mu = 0.33$) underline this tendency.

At the high-temperature side, measurements were carried out in and above the range of the glass transition. In the experiments at 100, 120 and 150°C the rejuvenation temperature was raised to 180°C. This temperature may be considered to be sufficiently high for erasing ageing effects of the amorphous regions with restricted mobility, while crystallization effects are still expected to be vanishingly small. As may be expected, the creep curves at 100°C and, to a lesser extent, at 120°C reflected the proximity of the glass transition. Apart from deviant behaviour at the lowest creep times, a smaller curvature was observed (γ values of 0.08 and 0.15 respectively). In analogy to flexible polymers[2], vertical shifts had to be included in the fitting procedures above T_g. The vertical shift is characterized by the associated shift rate β:

$$\beta = \frac{\mathrm{d}\log J}{\mathrm{d}\log t_e} \tag{4}$$

In this relation the compliance J refers to corresponding points on the creep curves of different age. The experimental data and best-fit curves at 150°C, where the influence of T_g has disappeared, are given in *Figure 5*. Again, simultaneous fitting of all curves took place, leading to only one adjustable value of each KWW parameter (J_0 and t_0 values given at ageing time of 1 h). The modified behaviour with regard to the vertical shifting, as compared to the results below T_g, is apparent. The curvature exponent of the compliances again amounts to $\gamma \simeq 0.2$. The horizontal shift rate μ shows a steady decrease with temperature in the region around and above T_g. The interpretation of the vertical shift (the negative value of β corresponds to a stiffness increase) is not straightforward. Since physical ageing in semicrystalline polymers is associated with a distribution of T_g values in a wide range above the actually observed transition (extended glass transition model), it may be viewed as resulting from vitrification of a minor amorphous fraction. Alternatively, it may also be interpreted as a crystallization effect. The interference with crystallization is clearly displayed in *Figure 6*. *Figure 6a* contains the results of creep measurements at 180°C without any pretreatment at a higher temperature, while the data of *Figure 6b* (same scale) were obtained after a 'rejuvenation' of 30 min at 210°C. At 210°C, small but distinct (re-)crystallization effects may be anticipated, and the effect on the creep behaviour is obvious: both the horizontal and the vertical shift rate are reduced substantially and the overall creep is diminished. Note that KWW fitting yields good results in all cases and that both γ and J_0 turn out to be virtually unaffected by crystallinity. In view of these findings at 180°C it may be inferred that also at somewhat lower temperatures crystallization-related phenomena are involved in the observed (creep as well as ageing) time dependences.

For the description of the effects of physical ageing on the mechanical properties, the key parameter is the horizontal shift rate. *Figure 7* displays the temperature dependence of this shift rate in the investigated range, as derived from the outlined fitting procedures. From this figure, the most prominent region for physical ageing

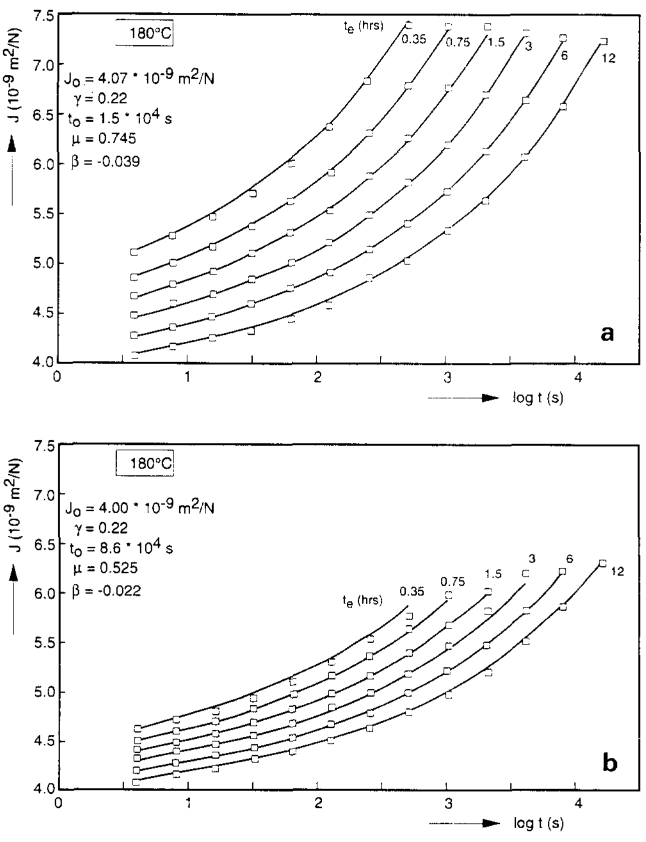

Figure 6 Experimental data at 180°C without preceding heating to a higher temperature (a) and after 0.5 h at 210°C (b). Full curves result from fitting

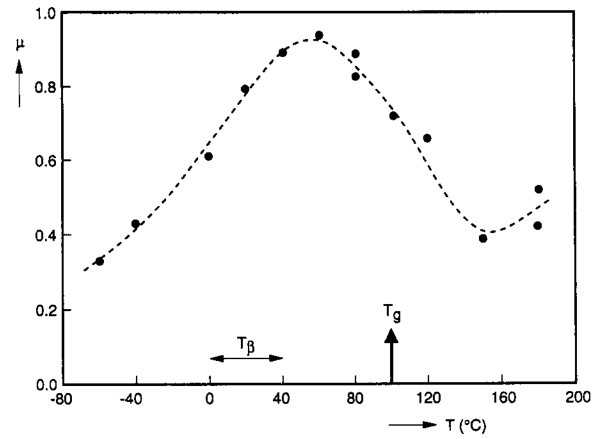

Figure 7 Temperature dependence of the observed horizontal shift rate

in the Vectra polymer becomes evident in relation to the transition temperatures. Comparison of the observed behaviour of μ vs. T with similar research on semicrystalline flexible polymers[2] (e.g. polypropylene (PP)) reveals a large resemblance. Even the onset to increase at the upper limit of the investigated temperature range is reproduced in flexible polymers. The qualitative interpretation of the temperature dependence of physical ageing, as proposed for semicrystalline flexible polymers, may therefore be adopted for liquid-crystalline random copolymers.

CONCLUSIONS

The present investigation has shown that the effects of physical ageing on mechanical creep in the liquid-crystalline copolyester Vectra A900, as monitored by the time- and temperature-dependent shifting behaviour, are essentially the same as those found in flexible polymers. In a wide temperature range the creep curves could be described very well by the familiar KWW relation; only around room temperature and around 100°C (secondary and glass transition respectively) do some deviations at low creep times occur. A notable difference was encountered in the curvature of the creep compliances. At most temperatures we derived a curvature exponent $\gamma = 0.20 \pm 0.02$, a value distinctly smaller than reported for flexible polymers. At the lowest temperatures investigated and in transition regions, an even lower value was found. Since the time dependence of the short-term creep is itself determined by molecular mobility, this might indicate some specific influence of the LC ordering on a microscopic level. With regard to crystallization effects, it was observed that these may significantly interfere with physical ageing far enough above T_g. However, also in this respect no specific discrepancy with flexible polymers could be concluded.

Concerning the possibly different nature of the glass transition, it can be stated that the investigation provided no evidence in this direction. The observed rejuvenation behaviour and the characteristics of physical ageing below and above T_g are in line with a normal glass transition. The magnitude and temperature dependence of the observed ageing effects are fully comparable to flexible polymers. Considering the fact that volume effects in this kind of LC polymer are at least one order of magnitude smaller, this might have severe consequences for the interpretation of physical ageing as resulting from free-volume relaxations. A reconsideration of the driving force behind physical ageing seems necessary, at least in the case of LC random copolymers. For these specific polymers, the explanation is expected to be intimately related to the crystalline structure at a molecular level and the associated changes therein induced by time or temperature. Only by knowledge of the differences between amorphous and crystalline packing on a molecular scale could the rearrangement processes be interpreted more soundly in terms of physical ageing or crystallization. In this respect, non-periodic layer models or paracrystalline lattices as evoked for the understanding of crystallization phenomena in LC random copolymers[20-22] might also be helpful for the description of reordering in the amorphous fraction. Eventually, it might turn out that the difference between crystalline and amorphous structures (and changes herein) in these polymers is not so well defined as in flexible polymers.

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REFERENCES

1 Struik, L. C. E. 'Physical Ageing in Amorphous Polymers and Other Materials', Elsevier, Amsterdam, 1978
2 Struik, L. C. E. *Polymer* 1987, **28**, 1521, 1533; 1989, **30**, 799, 815
3 Cao, M.-Y. and Wunderlich, B. *J. Polym. Sci., Polym. Phys. Edn.* 1985, **23**, 521
4 Sauer, T. H., Zimmermann, H. J. and Wendorff, J. H. *Colloid Polym. Sci.* 1987, **265**, 210
5 Bechtoldt, H., Wendorff, J. H. and Zimmermann, H. J. *Makromol. Chem.* 1987, **188**, 651
6 Warner, S. B. *Macromolecules* 1980, **13**, 450
7 Chiou, J. S. and Paul, D. R. *J. Polym. Sci., Polym. Phys. Edn* 1987, **25**, 1699
8 Hedmark, P. G., Dick, R. W. R. and Gedde, U. W. *Polym. Bull.* 1990, **23**, 83
9 Blumstein, R. B., Kim, D. Y. and McGowan, C. B. *Am. Chem. Soc. Symp. Ser.* 1990, **435**, 294
10 McGowan, C. B., Kim, D. Y. and Blumstein, R. B. *Macromolecules* 1992, **25**, 4658
11 Butzbach, G. D., Wendorff, J. H. and Zimmermann, H. J. *Makromol. Chem., Rapid Commun.* 1985, **6**, 821
12 Hsiao, B. S., Shaw, M. T. and Samulski, E. T. *J. Polym. Sci., Polym. Phys. Edn* 1990, **28**, 189
13 Walsh, D. J., Dee, G. T. and Wojtkowski, P. W. *Polymer* 1989, **30**, 1467
14 Naumann, M., Underhill, R., Duran, R. S., Krücke, B., Diele, S. and Kuschel, F. *Makromol. Chem., Rapid Commun.* 1992, **13**, 243
15 Cheng, S. Z. D. *Macromolecules* 1988, **21**, 2475; Cheng, S. Z. D., Janimak, J. J., Zhang, A. and Zhou, Z. *Macromolecules* 1989, **22**, 4240
16 Kamal, M. R., Khennache, O. and Goyal, S. K. *Polym. Eng. Sci.* 1989, **29**, 1089 and references therein
17 Kachidza, J., Serpe, G. and Economy, J. *Makromol. Chem., Macromol. Symp.* 1992, **53**, 65
18 Levita, G. and Struik, L. C. E. *Polymer* 1983, **24**, 1071
19 Troughton, M. J., Davies, G. R. and Ward, I. M. *Polymer* 1989, **30**, 58
20 Hanna, S., Lemmon, T. J., Spontak, R. J. and Windle, A. H. *Polymer* 1992, **33**, 3
21 Hanna, S. and Windle, A. H. *Polymer* 1988, **29**, 207
22 Biswas, A. *J. Polym. Sci., Polym. Phys. Edn* 1992, **30**, 1375