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Thermorheological Simplicity and Fragility of Azobenzene Nematogenic Side-Chain Polymers

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Summary: The linear viscoelastic response of polymers from a nematogenic azobenzene methacrylate and its copolymers with nonmesogenic methyl methacrylate was studied. These samples showed thermorheological simplicity in the whole investigated temperature range, even across the nematic-isotropic transition. The temperature dependence of the zero-shear viscosity confirmed a thermorheologically simple behavior, which allowed interpretation of $\eta(T)$ in the framework of free-volume theory. The way the relaxation mechanisms tended to their asymptotic behavior was described in terms of fragility parameters, and a comparison of fragilities of the samples was carried out. The analysis of fragility and temperature dependence of viscosity provided better understanding of the way the architecture of these nematic polymers influences free-volume quantities and determines relaxation mechanisms.

Keywords: fragility; liquid-crystalline polymers; relaxation; rheology

Introduction

Side-chain liquid crystalline polymers have proved to be suitable materials as media for optical information storage. In particular, polymers containing photoresponsive azobenzene side groups showed great potential for application.[1] Optical writing from macroscopic to nanoscopic length scales was accomplished, for example, in the nematic polymethacrylate PMA4 system, either homopolymers or copolymers with methyl methacrylate (MMA), which consist of a spaced azobenzene side group as both nematogenic and photoresponsive unit (Figure 1).[2,3]

Achieving an effective, high-resolution, and long-term data storage deals with crucial parameters such as bit stability, homogeneity at molecular level, and working temperature.[2,3] Therefore, a comprehensive characterization of the polymeric matrix should employ different spectroscopic techniques that can cover several length and time scales. Accordingly, we used electron spin resonance (ESR) spectroscopy to study the stability of different molecular sites and their correlation times as a function of temperature in PMA4 homopolymers and copolymers.[2] Moreover, differential calorimetry investigations evidenced the occurrence of a peculiar transition in PMA4 homopolymers. Electron spin resonance techniques suggested that this transition is due to a conformational change of the polymer backbone driven by the increasing nematic order in the side groups.[2] On the other hand, rheology is fundamental in studying the mechanical behavior of these optical substrates, and determining the working temperature, because, in particular, terminal relaxation could affect bit stability.

In the present paper, results of linear viscoelastic studies on PMA4 homo- and copolymers are presented and discussed. The samples behaved in a thermorheologically

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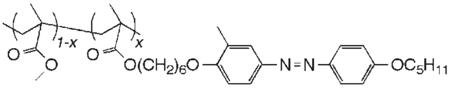

Figure 1.
Structure of PMA4 homopolymer ($x = 1$), 10/90, 20/80, 30/70 and 40/60 copolymers ($x = 0.9$, 0.8, 0.7, 0.6, respectively), and PMMA homopolymer ($x = 0$).

simple way and the time-temperature superposition (TTS) principle was found to hold over the whole investigated temperature range. The temperature dependence of the zero-shear viscosity of the polymers was also worked out and related to their dynamic fragility. A comparison of parameters determining the temperature behavior of terminal relaxation in the framework of free-volume theories also allowed one to emphasize the role played by the polymer architecture in affecting the mechanical response of the polymer matrix.

Materials and Experimental

The PMA4 samples under investigation are nematic polymethacrylates containing the (3-methyl-4′-pentyloxy)azobenzene mesogenic unit connected at the 4-position by a hexamethylene spacer to the main chain (Figure 1). The methacrylate monomer (MA4) was synthesized following a standard procedure.[4] Two PMA4 homopolymers (S1, S5) were prepared in polymerization batches in which the experimental conditions (concentration of monomer, initiator, and chain transfer agent, polymerization time) were adjusted to obtain samples with different molar masses (Table 1). Four random copolymers (C1-C4) were also synthesized from comonomer feed mixtures with different contents of non-mesogenic MMA counits (Figure 1: $x = 0.9, 0.8, 0.7, 0.6$, respectively).

Average molar masses (Table 1) were determined by size exclusion chromatography of chloroform solutions with a Waters 590 cromatograph, which was equipped with two Shodex KF804 columns and both Waters R401 RI and Perkin-Elmer LC75 UV detectors, and of chloroform and tetrahydrofuran solutions with a Jasco PU-1580 chromatograph equipped with two PL gel 5 μm Mixed-C and Mixed-D columns and both Jasco 830-RI and Perkin-Elmer LC75 UV detectors. Differential scanning calorimetry measurements were performed with a Perkin-Elmer DSC7 calorimeter (10 K/min heating rate) frequently calibrated with indium and zinc standards. The glass transition temperatures T_g, the nematic-isotropic temperatures T_{NI}, the onset temperature T_c of the conformational transition in the homopolymer backbone are reported in Table 1.[2] A detailed analysis of the molar mass and molar mass distributions of nematic azobenzene polymethacrylates was previously performed.[5] It was shown that neither T_g, T_{NI} or T_c were affected to any significant extent over the broad range of M_n and M_w/M_n investigated.

Rheological measurements were carried out with a Haake RheoStress RS150H rheometer with plane-plate sensor (20 mm diameter). The temperature was varied under highly pure nitrogen flow. In order to

Table 1.
Average molar masses and transition temperatures of the PMA4 samples.

Sample	x	M_n (g/mol)	M_w (g/mol)	M_w/M_n	T_g (K)[a]	T_c (K)[a]	T_{NI} (K)[a]
S1	1.0	18600	59000	3.17	294	320	353
S5	1.0	29900	72600	2.43	305	337	357
C1	0.9	53000	180000	3.40	306	–	352
C2	0.8	49000	177000	3.61	308	–	348
C3	0.7	33000	117000	3.54	314	–	346
C4	0.6	23250	93200	4.01	320	–	–[b]

[a] The T_g was evaluated according to the enthalpic definition.[6] The T_c and T_{NI} were evaluated according to the onset definition.[6]

[b] The C4 copolymer did not show T_{NI} in DSC scans, but a dynamic transition at nano-length scale could be inferred by ESR measurements at 353 K.[7]

account for thermal dilatation of the system, the gap in the plane parallel geometry was automatically varied in the temperature range between 0.40 mm and 0.60 mm. The gap was chosen to ensure gap-independent measurements. A Haake TC501 thermo-controller unit kept the temperature of the sample stable within 0.1 K. Preliminary tests ensured that all measurements were carried out in the linear viscoelastic regime.

Results and Discussion

The PMA4 homo- and copolymers showed superimposable dynamic moduli G^* as a function of the damping factor $\tan\delta = G''/G'$ at temperatures below and above the nematic-isotropic transition, and even across the phase transition temperature T_{NI} (Figure 2). This finding evidences that the PMA4 samples behaved in a thermorheologically simple way. Failures of the TTS principle have been found in main-chain liquid crystalline polymers, while nematogenic side-group polymers show failures of the TTS at very high molar masses.[8] TTS also held in similar polymethacrylates and polyacrylates with mesogenic azobenzene side-groups with comparable weight-average molar masses.[9] Despite the high molar mass, those polymers appeared to be unentangled.

Also the PMA4 samples of this work showed unentangled master curves (for example C3 in Figure 3), where quite parallel loss and storage modulus master curves are observed over a wide frequency range, following the power law $G' \sim G'' \sim \omega$. This behavior is expected in the modified Rouse theory for undiluted polymers and is a known property for polymers with molar masses near the minimum values for entanglement coupling in the region between the terminal and the glassy zones.[10] In various acrylic polymers such a rubbery plateau, characteristic of an entangled dynamics, first appears roughly at the critical molar mass $M_c' \sim 3M_e \sim 150$ Kuhn segments,[11] with M_e the entanglement mass. The lack of such a plateau in these side-group nematic polymers is ascribed to the mesophase order that would dilate the confining tube, on which dimension the M_e value depends,[9,11] and shift entanglement to higher molar masses.

According to TTS, the dependence of the shear dynamic modulus G^* on pulsation ω and temperature can be written as a function of the modulus measured at the reference temperature T_r [12]:

$$G^*(\omega, T) = b_{Tr}(T)G^*(\omega a_{Tr}(T), Tr) \tag{1}$$

The vertical $b_{Tr}(T)$ and horizontal $a_{Tr}(T)$ shift parameters are two real temperature-dependent functions. The $a_{Tr}(T)$ factor strongly depends on temperature and follows the Williams-Landel-Ferry law (WLF)[10]:

$$-\log a_{Tr}(T) = \frac{C_1(T - T_r)}{C_2 + T - T_r} \tag{2}$$

The C_1, C_2, and T_r parameters are given in Table 2.

The temperature dependence of the viscosity showed no evidence of discontinuity (Figure 4), not even for the copolymers at T_{NI}. The viscosity data were fitted by means of a Vogel-Fulcher law (VF):

$$\eta = \eta_\infty \exp\left(\frac{T_b}{T - T_0}\right) \tag{3}$$

The values of the pseudo-activation energy T_b, the Vogel temperature T_0, and the factor η_∞ are given in Table 3.

For thermorheologically simple materials it can be verified that VF parameters can be related to T_r-invariant parameters of WLF by means of[13]:

$$\begin{aligned} C_1 C_2 \ln 10 &= T_b, \\ T_r - C_2 &= T_0. \end{aligned} \tag{4}$$

The VF and WLF fit parameters for the PMA4 samples confirmed the validity of these relationships (Table 3). This further supports the conclusions on the thermorheological simplicity of PMA4 samples, and that the rheological properties of these materials are dominated by the polymer backbone.[8] Further WLF invariants can be obtained removing any dependence on

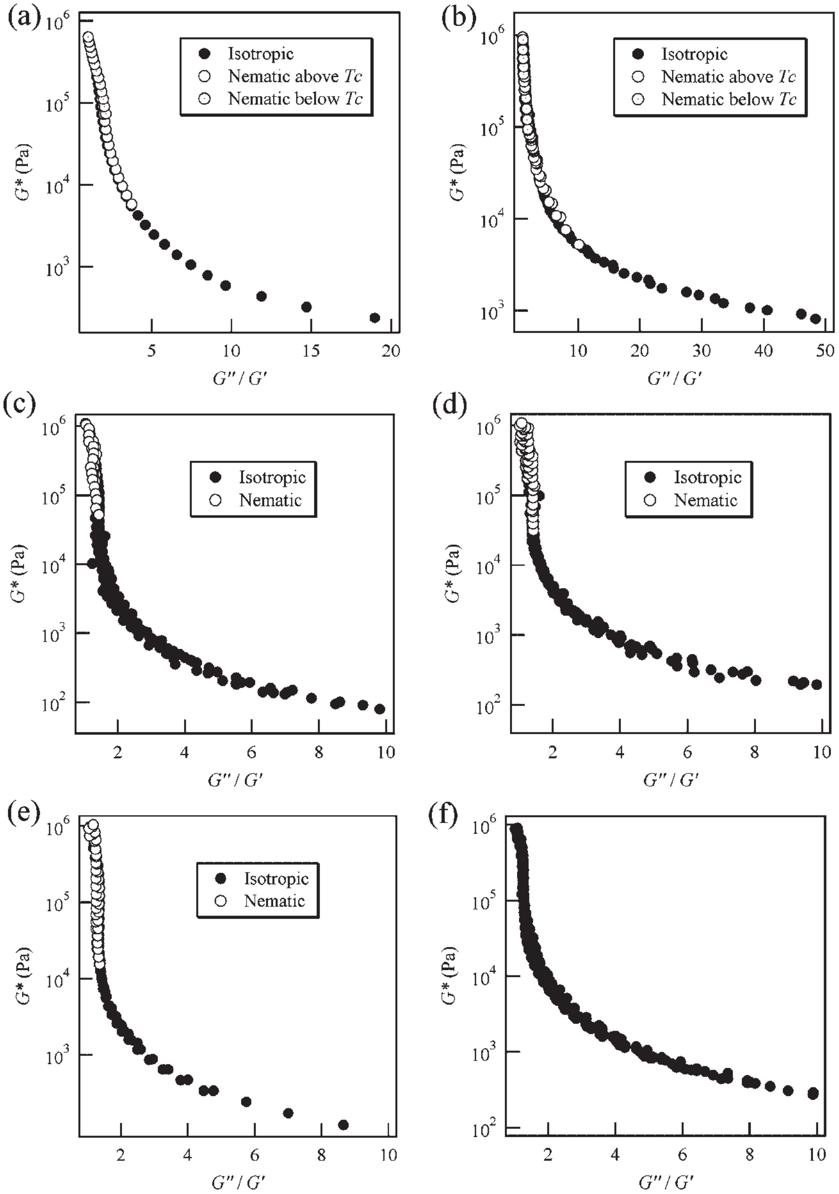

Figure 2.
The dynamic modulus G^* of the PMA4 samples as a function of the damping ratio tan $\delta = G''/G'$ shown to be superimposable at different temperatures, even across the T_{NI}: S1 (a), S5 (b), C1 (c), C2 (d), C3 (e), C4 (f).

polymer chain mobility in C_1 and C_2, being C_1C_2 and $T_r - C_2$ constants independent of T_r, by extrapolating the parameters C_1^g and C_2^g at T_g [10] (Table 3).

According to Doolittle equation,[14] VF and WLF parameters can be expressed in terms of the free-volume ratio f, the thermal expansion coefficient of the free volume α, and a coefficient B by Eq. 4 and

$$C_1 = \frac{B}{f(T_r)\ln 10} \qquad C_2 = \frac{f(T_r)}{\alpha}. \tag{5}$$

Another key quantity characterizing the temperature dependence of the viscosity is

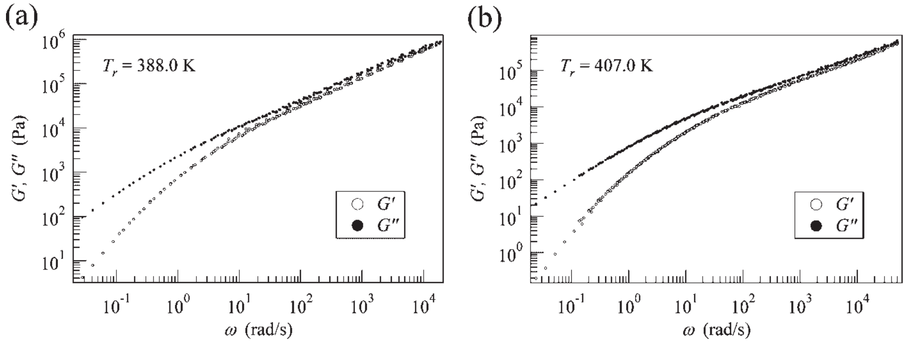

Figure 3.
Master curves of the storage G' (empty circles) and loss G'' (filled circles) moduli of the C3 (a) and C4 (b) copolymers.

the fragility. Various methods have been suggested in literature to evaluate the fragility of a polymer, which characterizes the way by which the temperature modifies the properties of a given material.[15] The relaxation mechanisms of fragile polymers follow a VF behavior, while strong polymers tend to follow an Arrhenius dependence. Thus, when writing the VF law as

$$\eta = \eta_\infty \exp\left(\frac{DT_0}{T - T_0}\right), \tag{6}$$

the $D = T_b/T_0$ parameter is often used to indicate the fragility of a polymer.[15] The greater D is, the stronger the polymer is. In the limit for D tending to infinity, Eq. 6 becomes an Arrhenius-like activated process. In the free-volume theory framework, it results (Eqs. 4 and 5)

$$D = \frac{T_b}{T_0} = \frac{B}{\alpha T_g - f(T_g)}. \tag{7}$$

Another way to evaluate the fragility of a polymer is to plot viscosities in a rescaled Angell-like plot,[16] where the rescaled viscosity

$$\exp\left(\frac{\ln(\eta(T)/\eta(T_g))}{\ln(\eta(T_g)/\eta_\infty)}\right) = \left(\frac{\eta(T)}{\eta(T_g)}\right)^{\frac{T_g - T_0}{T_b}} \tag{8}$$

is plotted vs. T_g/T. From such a plot, one can examine how the relaxation mechanisms of the polymer tend to their asymptotic behavior. In particular, according to the Doolittle equation, this plot represents the temperature dependence of the free volume ratio function $f(T_g)/f(T) - 1$, and its curvature (fragility) is sensitive to the ratio $\kappa = T_g/(T_g - T_0)$. According to Eqs. 4 and 5, the curvature can be written as

$$\kappa = \frac{T_g}{T_g - T_0} = \frac{T_g}{f(T_g)/\alpha}. \tag{9}$$

Another parameter, apparently more local,

$$m = \left.\frac{d\log\tau}{d(T_g/T)}\right|_{T=T_g} = \frac{1}{\ln 10}\,\frac{T_b T_g}{(T_g - T_0)^2} = T_g \frac{C_1^g}{C_2^g} \tag{10}$$

is the dynamic fragility m, also referred to as steepness index.[15,16] As it accounts for the slope of the dynamic behavior of relaxation process at T_g, not necessarily *a priori* correlations between m, D and κ can be expected, but in the framework of free-volume

Table 2.
WLF parameters of the PMA4 samples.

Sample	C_1	C_2 (K)	T_r (K)
S1	9.2 ± 0.1	60 ± 1	322.0 ± 0.1
S5	8.0 ± 0.1	60 ± 1	338.0 ± 0.1
C1	6.0 ± 0.1	89 ± 1	363.0 ± 0.1
C2	7.5 ± 0.1	85 ± 1	353.0 ± 0.1
C3	5.7 ± 0.1	122 ± 2	388.0 ± 0.1
C4	5.9 ± 0.1	149 ± 2	407.0 ± 0.1

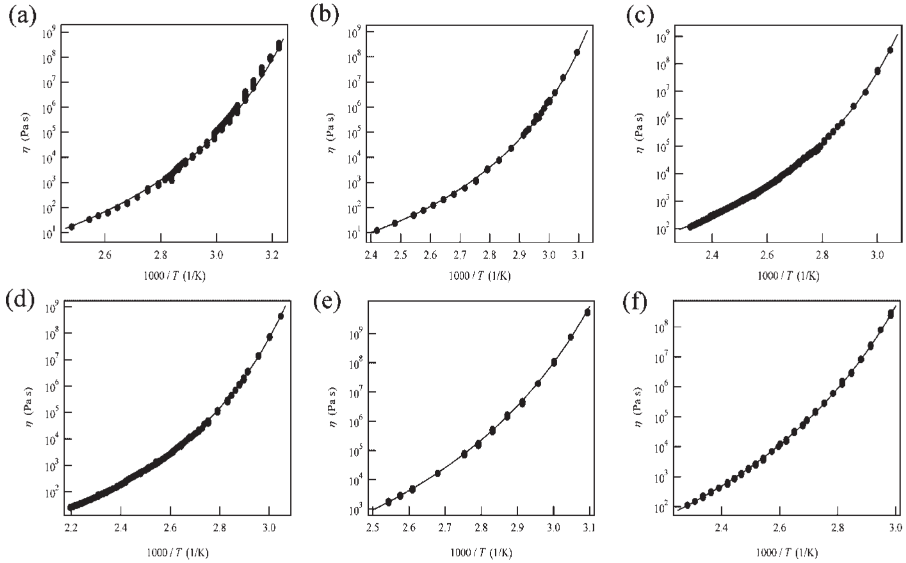

Figure 4.
Zero-shear viscosity for the S1 (a) and S5 (b) homopolymers, and C1 (c), C2 (d), C3 (e), and C4 (f) copolymers with superimposed VF fits (continuous lines).

theories it results

$$m = T_g \frac{C_1^g}{C_2^g} = \frac{T_g}{f(T_g)/\alpha} \frac{B}{f(T_g)}. \qquad (11)$$

Therefore, it is apparent that all the three fragility parameters D, κ, and m are determined by the same three microscopic quantities $f(T_g)$, B, and α. Nevertheless, it should be noted how the measurement of T_g is determinant in evaluating these quantities. On the other hand, even if often m has been correlated to the thermodynamic steepness index, as defined in terms of the variation of the specific heat at the glass transition $\Delta C_p(T_g)$, no clear connections between thermodynamic and dynamic steepness index have been found yet.[17]

Experimental viscosity data and VF fits of the PMA4 S5 homopolymer, and C1-C4 copolymers are shown in the rescaled Angell plot in Figure 5. The inset of the Figure shows the whole theoretical temperature range. The rescaled Angell plot for a conventional literature PMMA homopolymer[18] is also shown in Figure 5. The fragility parameters D, κ, and the dynamic fragility m of the copolymers, the PMA4 homopolymers and the literature PMMA are reported in Table 4, together with the respective T_g.

A clear trend from the strongest PMMA sample to the most fragile PMA4 homopolymer can be observed in Table 4 and Figure 5. In this behavior, the influence of the molar mass on the fragility can be

Table 3.
VF parameters of the PMA4 samples and WLF T_r-invariants.

Sample	η_∞ (Pa s)	T_b (K)	T_0 (K)	C_1C_2 ln10 (K)	$T_r - C_2$ (K)	C_1^g	C_2^g (K)
S1	$(2.2 \pm 0.1) \times 10^{-3}$	1300 ± 30	259 ± 5	1270 ± 30	262 ± 1	18 ± 2	30 ± 2
S5	$(3.7 \pm 0.1) \times 10^{-3}$	1100 ± 30	278 ± 3	1100 ± 40	278 ± 1	18 ± 2	27 ± 2
C1	$(5.1 \pm 0.6) \times 10^{-3}$	1240 ± 40	274 ± 3	1230 ± 30	274 ± 1	17 ± 2	31 ± 3
C2	$(8.8 \pm 0.8) \times 10^{-3}$	1480 ± 60	268 ± 3	1470 ± 40	268 ± 1	16 ± 2	40 ± 3
C3	$(7.5 \pm 0.3) \times 10^{-3}$	1570 ± 30	266 ± 2	1600 ± 50	266 ± 2	14 ± 2	48 ± 4
C4	$(2.0 \pm 0.2) \times 10^{-3}$	1960 ± 50	258 ± 2	2000 ± 70	258 ± 2	14 ± 2	62 ± 4

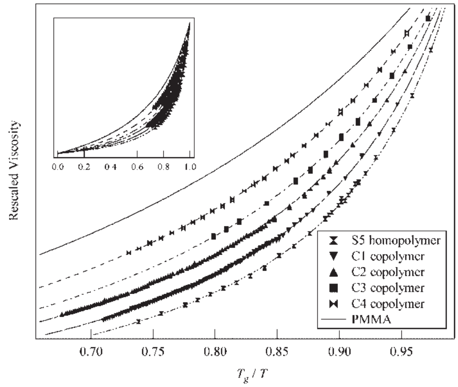

Figure 5.
Rescaled Angell plot (Eq. 8) of the PMA4 samples. The rescaled temperature behavior of the viscosity of a conventional literature PMMA homopolymer[18] is also shown.

confidently ruled out, the four copolymers having comparable M_w/M_e ratios,[19] and S5 exhibiting a M_w value sufficiently high. On the other hand, the fragility increases with the molar mass for the PMA4 homopolymers (Table 4). This fact well agrees with the trend of Figure 5, even if the homopolymers have average molar masses lower than the ones of the copolymers.

Therefore, the observed trend of the fragility is in agreement with the one expected in going from more to less symmetric main chain structure,[20] as determined by incorporation of the side groups in copolymers. Moreover the side chains also affect the rigidity of the polymer main chain as revealed by the values of the glass transition temperature, that increase from fragile PMA4 to strong PMMA. A correlation can be then inferred between the enhanced rigidity of the polymer chain and the stronger character of the system.[21] Moreover, it should be recalled that for a great majority of polymer systems, $f(T_g) = 0.025 \pm 0.005$.[10] The view that the free volume at T_g should be a constant was first introduced by Fox and Flory.[22] This fact and the results for C_1^g in Table 3 suggest that B varies smoothly in the PMA4 samples, showing a variation of the 30% from PMMA[18] to PMA4 homopolymers. The variation of B may be associated with differences in the minimum hole size required for local segmental motions.[10,14] On the other hand, the values of α are known to show considerably more variation.[10] In fact, $C_2^g = f(T_g)/\alpha$ (Table 3) triplicates its value monotonically from PMMA[18] to PMA4. The longer side group increase the thermal expansion coefficient of the free volume of the PMA4 samples.

Table 4.
Fragility parameters D, κ, and m (Eqs. 7, 9, and 11) of the PMA4 samples. Data of a conventional literature PMMA homopolymer[18] are also given.

Sample	D	κ	m	T_g (K)
S5	4.0 ± 0.2	11.3 ± 0.3	190 ± 9	305
S1	5.0 ± 0.3	8.8 ± 0.4	175 ± 9	294
C1	4.5 ± 0.2	9.6 ± 0.3	162 ± 7	306
C2	5.5 ± 0.3	7.7 ± 0.3	123 ± 7	308
C3	5.9 ± 0.3	6.5 ± 0.2	92 ± 6	314
C4	7.6 ± 0.4	5.2 ± 0.2	72 ± 5	320
PMMA	12.3 ± 0.7	3.8 ± 0.3	56 ± 5	390

Conclusions

The rheological response of different PMA4 homo- and copolymers in the linear viscoelastic regime has been investigated. These materials behaved in a thermorheologically simple way, and the TTS principle held in the overall range of temperature. Comparison between VF fitting parameters and WLF invariants provided further evidence that the rheological properties of the polymers were dominated by the structure of their main-chain backbone. Nevertheless, the effects of the side groups were recognized in the absence of an entangled regime for the molar masses under investigation.

Moreover, the increasing fragility from the strongest PMMA to the PMA4 homopolymer was connected with the symmetry of the polymer architecture and the rigidity of the polymer main chain. A study of fragility parameters in the framework of free-volume theory also enlightened the role of the polymer architecture in dictating the relaxation properties of the PMA4 polymers.

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