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Linear Viscoelastic Behavior of an Azobenzene Nematic Block Copolymer

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We report on the rheological investigation of a nematic block copolymer of an azobenzene methacrylate (MA4) and methyl methacrylate (MMA). Relaxation processes are discussed in terms of chain architecture and viscoelastic response of the polymer. In contrast to analogous random copolymers of MMA and MA4, the present block copolymer did not show validity of the time-temperature superposition (TTS) principle for all material functions. TTS was found to work only for the storage modulus. Rheological steady-state and oscillatory measurements were thus compared in order to obtain further insight into such a peculiar phenomenon.

Keywords: azobenzene; block copolymer; liquid crystal; rheology; shear viscosity

1. Introduction

In the last years great attention has been paid to devices for optical information storage based on side-chain polymers, especially those containing photoresponsive azobenzene units [1–7]. The attainment of ultra-high density (foreseen up to 1 Tbyte/cm^2) optical data storage, *e.g.* for re-writable DVDs, requires the development of materials able to sustain stable modifications of their optical properties sized on the order of tens of nanometers, or even less. Besides new materials, research on nano-optical writing demands non-conventional optical schemes able to access sub-diffraction spatial resolution. To these aims, we recently investigated a copolymer system of methyl methacrylate (MMA) and a methacrylate carrying an azobenzene side-group (MA4) as nematogenic photoresponsive unit [5–14].

An effective, high-resolution and long-term data storage is possibly achieved only by controlling crucial parameters such as bit stability, homogeneity at molecular level, and working temperature [5, 6]. Therefore, a full knowledge of relaxation processes of the polymeric matrix is needed, which should employ different spectroscopic techniques that can cover several length and time scales. Accordingly, we used electron spin resonance spectroscopy and rheology to study the stability of different molecular sites, their correlation times, and viscoelastic relaxation times as a function of temperature in MA4 homopolymers and MMA-MA4 random copolymers [5–14]. Similar analyses have been extended

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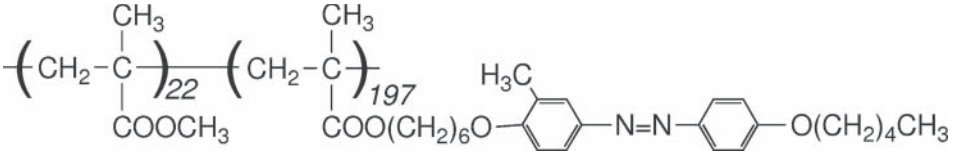

Figure 1. Sketch of the block copolymer B10 (10 mol% MA4).

to a newly synthesized MMA-MA4 block copolymer (B10) containing a relatively short azobenzene block (10 mol% MA4) (Figure 1).

Here we show the results of the linear viscoelastic characterization of B10 performed by means of creep-and-recovery experiments and oscillatory measurements. We found that the time-temperature superposition (TTS) principle does not hold for this block copolymer. Nevertheless, superposition of storage modulus was possible, allowing the detection and the comparison of different relaxation mechanisms that are discussed in terms of the polymer architecture.

2. Materials and Experimental

The B10 block copolymer was prepared by a sequence of two atom transfer radical polymerization (ATRP) steps, by which a MMA macroinitiator was first formed and then used to incorporate the second MA4 block. The experimental procedure will be detailed elsewhere [15]. The copolymer composition and the average degrees of polymerization were evaluated from the ^{1}H NMR spectra by using the known values for the MMA macroinitiator. The average molar masses and their dispersity were determined by size exclusion chromatography (SEC) with PMMA standards (Table 1). Differential scanning calorimetry (DSC) 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 for the MA4 and MMA blocks (T_g^{MA4} and T_g^{MMA}, respectively), and the nematic-isotropic transition temperature T_{NI} are also reported in Table 1.

Creep-and-recovery experiments and frequency sweep measurements were carried out with a Anton Paar Physica MCR301 torsional rheometer in the plane-plate geometry (25 mm diameter). A CTD450 temperature control unit kept the temperature of the sample stable within 0.1 K. Preliminary tests were conducted to ensure that all measurements were carried out in the linear viscoelastic regime.

3. Results and Discussion

The rheological measurements were performed in the temperature range 400–465 K. First of all, let us examine the response of oscillatory measurements. Frequency sweeps of complex

Table 1. Transition Temperatures and Molar Mass Dispersity of the Block Copolymer

T_g^{MA4} (K)	T_g^{MMA} (K)	T_{NI} (K)	M_w (g/mol)	M_w/M_n
323	397	353	34300	1.27

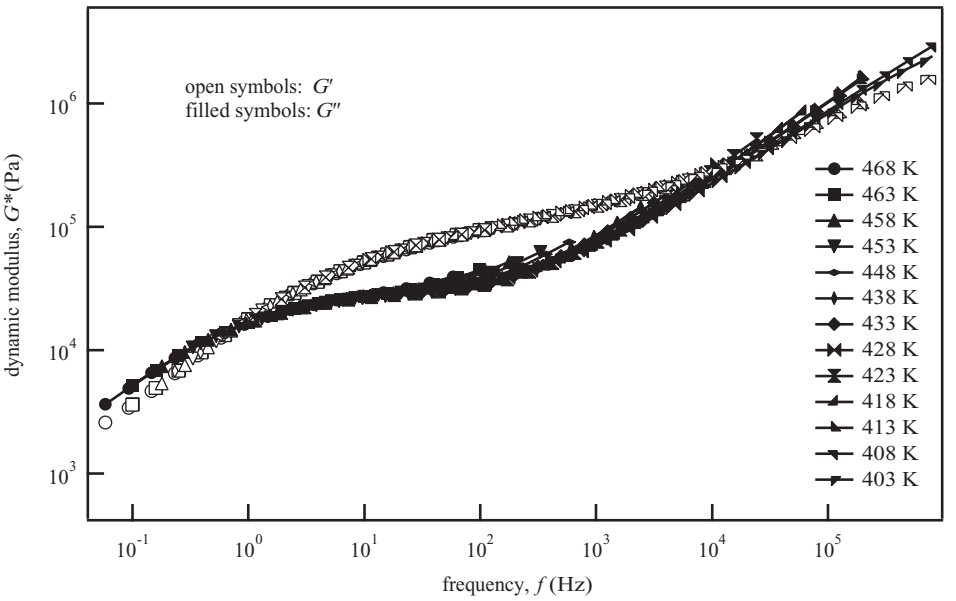

Figure 2. Frequency sweeps of storage (open symbols) and loss (filled symbols) moduli horizontally shifted in order to obtain a master curve of G' at the reference temperature $T_r = 463$ K.

shear modulus at different temperatures are shown in Figure 2. Data are horizontally shifted in order to build a master curve of G' and G'' according to TTS principle [16, 17]. It appears from inspection of Figure 2 that the loss modulus G'' frequency sweeps cannot be shifted to completely match measurements acquired at different temperatures in order to build a unique master curve. Instead, complete superposition of G' could be achieved.

In our previous investigations on the rheological response of MA4 homopolymers and MMA-MA4 random copolymers, we never found any failure of TTS, even for polymers with molar masses much higher than the M_w of B10 [18, and references therein]. Failure of the TTS principle in B10 has to be ascribed to the blocky nature of the copolymer. In fact, it is worth recalling that one way for the failure of TTS principle is when a different temperature scaling is found for relaxation mechanisms of the polymer chain. Therefore one can expect that the relaxation mechanisms of the two MA4 and MMA blocks along the main chain are driven by different mechanisms.

Let us interpret this behavior in terms of main-chain normal modes [19]. The linear viscoelastic frequency response of polymers can be described in terms of the superposition of different normal modes. The first normal mode represents relaxation mechanisms on the scale of the whole polymer chain. On increasing the index of the mode, the associated relaxation time decreases involving less and less counits along the chain. This means that in random copolymers, chain normal modes can be considered equal, on average, even when they involve a few counits for high mode index [19]. On the contrary, differences in architecture render the polymer sensitive to very low modes for B10. Nonetheless, a partial superposition was possible at lower frequencies, corresponding to higher relaxation times. This was because the lower is the frequency, the longer is the chain mode contributing to the polymer dynamics. Therefore, in this terminal region the monomeric friction coefficient of the polymer chain can be reasonably considered as an average of the friction coefficients of the MA4 and MMA blocks. The frequency response of the longest modes, which have almost the

same averaged friction coefficient, can be therefore superposed. On the contrary, the shorter modes originate from MMA or MA4 units only. This results in different temperature dependences of monomeric friction coefficients and inhibits the validity of the TTS principle.

Even though the TTS principle does not hold for the loss modulus G'', it was possible to build the master curve for the storage modulus G' shown in Figure 2 at the reference temperature $T_r = 463$ K. The fact that TTS holds for G' in the whole investigated range could be ascribed to the fact that blocky nature of the copolymer and different temperature dependences of the monomeric factors affect more the viscous properties of the material than the elastic ones. This can be naively explained considering that the polymer backbone has the same methacrylate nature in both blocks of the copolymer, which are instead differentiated for the side chains, mainly responsible for steric effects.

For comparison, the master curves of a random MMA-MA4 copolymer (70 mol% MA4) and a MA4 homopolymer are shown in Figure 3 [14, 18]. It is evident that the presence of the MMA block makes the shear modulus of the block copolymer greater in a wide frequency range, even though the average weight molar mass of the block copolymer is much lower than that of both the random copolymer and homopolymer. Moreover, the MMA block, whose molar mass is larger than the entanglement mass [20] of PMMA (about 9000 g/mol), also determines a rubbery plateau in frequency sweeps of the block copolymer, which instead is missing in other even higher molar mass random MMA-MA4 copolymers and MA4 homopolymers [14, 18]. In these systems, the lack of the entanglement plateau was ascribed to the nematic order which dilates the confining tube and shifts the entanglement to higher molar masses [18].

Evidence that the elastic and viscous behaviors of the block copolymer are driven by different mechanisms is also provided by comparison between the viscosity evaluated by creep-and-recovery experiments and the shift factors obtained by construction of storage modulus master curve (Figure 4). According to TTS, the dependence of the shear elastic complex modulus G^* on the frequency f and the temperature T can be written as a function of the shear elastic complex modulus measured at the reference temperature T_r [16, 18, 21]:

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

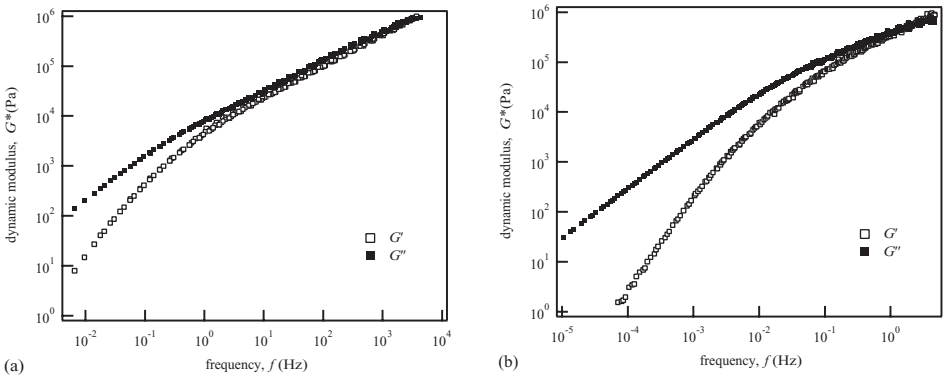

Figure 3. Master curves of a random MMA-MA4 copolymer (70 mol% MA4) (a) and a MA4 homopolymer (b) at $T_r = 388$ K and 338 K, respectively [14, 18].

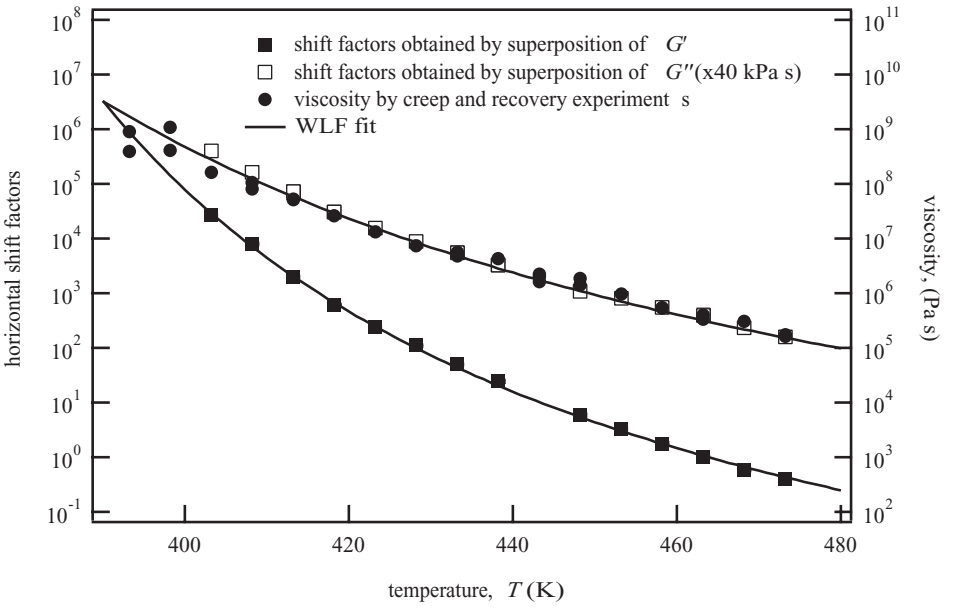

Figure 4. Temperature dependence of: viscosity evaluated by creep-and-recovery experiments (circles), shift factors obtained by construction of G' master curve (filled squares), and shift factors obtained trying to overlap the high-frequency side of G'' frequency sweeps (empty squares). WLF fit parameters (Eq. (2)) are given in Table 2.

The vertical and horizontal shift factors, $b_{Tr}(T)$ and $a_{Tr}(T)$, are two real temperature-dependent functions. The $a_{Tr}(T)$ factor strongly depends on temperature and follows the Williams-Landel-Ferry (WLF) law [16, 18, 21]:

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

Master curves and horizontal and vertical shift factors at the reference temperature are obtained by means of a numerical shift of the experimental isothermal frequency sweeps of the dynamic modulus [17].

When TTS holds, horizontal shift factors and zero shear viscosity are expected to have the same temperature dependence described by a WLF law [16, 21, and references therein]. This is not the case for B10. In fact, inspection of Figure 4 shows how shift factors obtained building the master curve of G' follow a WLF law, but viscosity follows a different temperature behavior (Figure 4). This finding supports the idea of different mechanisms driving the viscous and elastic responses of the block copolymer. A profitable comparison could be expected between viscosity and G''. Therefore, since the viscous behavior of a sample is determined by the G'' modulus, we tried to overlap the high-frequency side of G'' frequency sweeps obtaining the shift factors shown as open squares in Figure 4. Their temperature dependence is similar to that of viscosity. WLF parameters obtained fitting horizontal shift factors and viscosity data of Figure 4 are given in Table 2. Fit parameters of shift factors obtained building the master curve of G' are comparable with WLF parameters found for PMMA homopolymers [16, 22].

Table 2. WLF Fit Parameters of Temperature Dependence of Viscosity and Shift Factors Obtained by Superposition of Storage and Loss Moduli

WLF parameters	C_1	C_2 (K)	T_r (K)
horizontal factors for G'	6.0 ± 0.1	140 ± 2	463
viscosity[(a)]	3.6 ± 0.2	220 ± 20	463
horizontal factors for G''	3.6 ± 0.1	220 ± 10	463

[(a)] WLF parameters for viscosity were obtained by mathematical equivalence of WLF and Vogel–Fulcher parameters [16].

4. Conclusions

Block architecture of the B10 block copolymer improves the thermal stability of the matrix increasing relaxation times of the melt with respect to analogous random copolymers. The dynamics of the polymer chains, which is complicated by the different monomeric friction coefficients of the two blocks, was interpreted in terms of chain structure and molar mass distribution. Comparison of the rheological response of block copolymers of different MA4 contents is planned in order to highlight and better evaluate the role of chain architecture in such a peculiar viscoelastic behavior. The block copolymer can be used as a photoresponsive matrix for optical data storage. Nano-writing experiments by scanning near-field optical microscopy (SNOM) are currently being carried out.

References

[1] Kreger, K., Wolfer, P., Audorff, H., Kador, L., Stingelin-Stutzmann, N., Smith, P., Schmidt, H.W. *J. Amer. Chem. Soc.*, **132**, 509 (2010).
[2] Gimeno, S., Forcen, P., Oriol, L., Piñol, M., Sánchez, C., Rodríguez, F.J., Alcalá, R., Jankova, K., Hvilsted, S. *Europ. Polym. J.*, **45**, 262 (2009).
[3] Naka, Y., Yu, H., Shishido, A., Ikeda, T. *Mol. Cryst. Liq. Cryst.*, **498**, 118 (2009).
[4] Yu, H., Kobayashi, T., Ge, Z. *Macromol. Rapid Commun.*, **30**, 1725 (2009).
[5] Galli, G., Szanka, I., Andreozzi, L., Autiero, C., Faetti, M., Giordano, M., Zulli F. *Macromol. Symp.*, **245–246**, 463 (2006).
[6] Andreozzi, L., Faetti, M., Galli, G., Giordano, M., Palazzuoli, D. *Macromolecules*, **34**, 7325 (2001).
[7] Likodimos, V., Labardi, M., Pardi, L., Allegrini, M., Giordano, M., Arena, A., Patanè, S. *Appl. Phys. Lett*, **82**, 3313 (2003).
[8] Andreozzi, L., Faetti, M., Giordano, M., Zulli, F., Galli, G., Laus, M. *Mol. Cryst. Liq. Cryst.*, **429**, 301 (2005).
[9] Andreozzi, L., Faetti, M., Giordano, M., Palazzuoli, D., Zulli, F., Galli, G. *Mol. Cryst. Liq. Cryst.*, **429**, 21 (2005).
[10] Andreozzi, L., Autiero, C., Faetti, M., Giordano, M., Zulli, F., Galli, G. *Mol. Cryst. Liq. Cryst.*, **450**, 363 (2006).
[11] Andreozzi, L., Faetti, M., Giordano, M., Zulli, F., Galli, G., Samaritani, S. *Mol. Cryst. Liq. Cryst.*, **450**, 373 (2006).
[12] Andreozzi, L., Autiero, C., Faetti, M., Giordano, M., Zulli, F., Szanka, I., Galli, G. *Mol. Cryst. Liq. Cryst.*, **465**, 25 (2007).
[13] Andreozzi, L., Faetti, M., Giordano, M., Zulli F. *Eur. Phys. J. B*, **41**, 383 (2004).
[14] Andreozzi, L., Autiero, C., Faetti, M., Galli, G., Giordano, M., Zulli, F. *Mol. Cryst. Liq. Cryst.*, **500**, 63 (2009).

[15] Galli G. *et al.* , in preparation.
[16] Ferry, J. D. *Viscoelastic Properties of Polymers*, Wiley: New York (1980).
[17] Honerkamp, J., Weese, J. *Rheol. Acta*, **32**, 57 (1993).
[18] Andreozzi, L., Autiero, C., Faetti, M., Galli, G., Giordano, M., Zulli, F. *Macromol. Symp.*, **263**, 78 (2008).
[19] Doi, M., Edwards, S. F. *The Theory of Polymer Dynamics*, Oxford University Press: Oxford (1986).
[20] Fetters L. J., Lohse D. J., Richter, D., Witten, T. A., Zirkel A. *Macromolecules*, **27**, 4639 (1994).
[21] Andreozzi, L., Castelvetro, V., Faetti, M., Giordano, M., Zulli, F. *Macromolecules*, **39**, 1880 (2006).
[22] Fuchs, K., Friedrich, C., Weese J. *Macromolecules*, **29**, 5893 (1996).