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Dynamic mechanical and thermal behavior of novel liquid-crystalline polybutadiene-diols with azobenzene groups in side chains

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Synopsis

Liquid-crystalline (LC) polymers containing methoxy- or butoxy-substituted azobenzene in side chains have been prepared via radical addition of the in advance synthesized nematic thiols onto double bonds of poly(butadiene)diol [Polakova *et al.*, Pol. Bull. **54**, 315–326 (2010)]. In the present work, thermal behavior of these comblike polymers has been characterized by differential scanning calorimetry and polarizing optical microscopy. LC transitions have been also determined by rheological measurement. Time–temperature superposition of mechanical functions has been successfully applied to samples undergoing direct nematic/glassy state transition. © 2013 The Society of Rheology. [<http://dx.doi.org/10.1122/1.4815980>]

I. INTRODUCTION

In the last few decades, thermotropic liquid-crystalline polymer (LCP) materials are attracting great attention, especially due to their unique potential in the field of technical applications. From LCPs, processable films could be made for photonic, ferroelectric and antiferroelectric applications, and second harmonic generation in nonlinear optics [Küpfer and Finkelmann (1991); Okano *et al.* (2005); Mysliwiec *et al.* (2011)]. LCPs usually consist of a polymer backbone and a mesogenic group. Mesogens can be bound on the polymer backbone (side chain LCPs) or can be incorporated directly in the polymer backbone (main chain LCPs). To synthesize a thermotropic side chain LCP, the

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designed molecule should obey special rules. The polymer backbone needs to be relatively flexible with a suitable glass transition temperature, T_g . Incorporation of the mesogenic units onto the polymer should not result in T_g greater than LC transition temperatures. To enable rigid mesogenic groups to form a mesophase, mesogens should be bound on the backbone through a flexible and sufficiently long spacer. Finkelmann *et al.* (1978) predicted that such spacer (usually consisted of more than 5 or 6 methylene units) contributes to effective decoupling of motions of mesogens involved in the ordered state from motions of the polymer segments.

The polymer nature of the LCPs allows for application of rheological methods for characterization of these materials. Ilavsky *et al.* (1998), Hotta and Terentjev (2003), Colby and Gillmor (1993), and many others used rheological measurements for characterization of LCPs. It was found that both temperature and frequency dependences of mechanical functions are sensitive to a presence of ordered LC structure due to more or less aligned parts in the macromolecule. Upon certain circumstances, frequency dependences of mechanical functions can be superimposed to obtain information about the sample behavior at conditions that are not accessible by a simple measurement.

We have synthesized novel types of LC thiols [Polakova *et al.* (2010)]. The structure of the thiols **MA** and **BA** is shown in Fig. 1. Both possess a *para*-substituted azobenzene as a mesogenic core and a thiol-terminated pentamethylene spacer attached by an ether bond to the mesogen. The synthesized mesogenic thiols have been grafted onto double bonds of commercially available poly(butadiene)diol Krasol LBH 3000 (PBD, Fig. 1) with varying initial mole ratio of thiol/double bonds (from 0.2 to 1.0). After a purification process, the structure and composition of the resulted comblike PBDs have been determined.

This present work is based on the detailed characterization of the thermal behavior of both the synthesized thiols and related comblike PBDs with respect to a mesophase formation. For the thermal behavior investigation, differential scanning calorimetry (DSC) and polarizing optical microscopy (POM) have been employed. Mechanical properties of the polymer samples (loss and storage moduli, loss tangent) have been determined using rheological measurements. Time–temperature superposition of the moduli and loss tangent has been successfully applied for some of these LC PBDs.

II. METHODS OF MEASUREMENTS

A. DSC

Calorimetric measurements were performed using a Pyris 1 DSC (Perkin–Elmer). Purge gas (helium) was let through the DSC cell with a flow rate of 20 ml/min. The

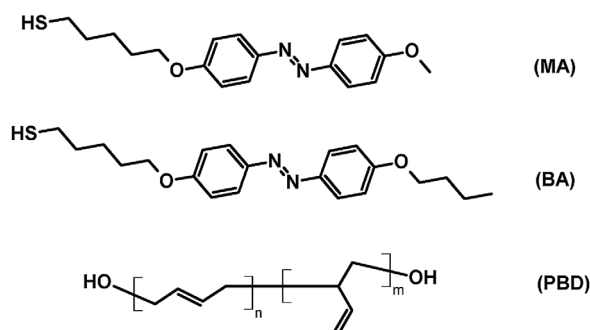


FIG. 1. The structure of the synthesized LC thiols **MA** and **BA** and the PBD used for the grafting reactions of these thiols.

temperature of the equipment was calibrated with mercury, H₂O, and indium. The melting heat of indium was used for calibrating the heat flow.

Samples of typical mass ca. 10 mg were first heated from 30 to 130 °C at 40 °C/min, held at 130 °C for 5 min, then subjected to a cooling scan to −60 °C at 10 °C/min, held at −60 °C for 15 min, and followed by a second heating scan to 130 °C at 10 °C/min. The reason, why the rate 10 °C/min was chosen, achieves in the nature of the poly(butadiene)-based polymers. As follows from our own experience, the higher heating/cooling rate, the better detectability of glass transition and mesophase transitions in these samples during DSC measurement.

B. POM

The texture of crystalline and LC phases and phase transition temperatures were determined by a POM Nikon Eclipse 80i equipped with a heating stage Linkam LTS350. The heating and cooling rates were 5 and 2 °C/min. These rates enabled us a better development of phase structures in grafted PBDs than the rate 10 °C/min used in DSC method.

C. Rheological measurement

Dynamic mechanical measurements were performed on a Bohlin CVOR 200 instrument with the parallel-plate geometry. Diameter of the used plates was 6 mm (for modulus higher than 10⁴ Pa), 15 mm (for modulus from 10⁴ to 10⁷ Pa), and 25 mm (for modulus lower than 10⁵ Pa). Both components of the complex shear modulus G^* ($G^* = G' + iG''$, where G' and G'' are the storage and loss modulus, respectively) and the loss tangent, $\tan \delta = G''/G'$, were determined.

Preparation of all polymer samples (measured with various plate diameters) was carried out by the following procedure. The polymer powder was placed between plates of the rheometer and heated until the isotropic state of the sample was reached.

Two types of measurements were made: Measurement of temperature dependence at constant frequency and isothermal frequency sweep. The temperature dependences of mechanical functions were measured at a constant frequency $f = 1$ Hz during cooling at the rate 2 °C/min; the strain was kept within a linear region of viscoelastic behavior. Isothermal measurements (frequency dependencies) of mechanical functions were made during the cooling regime. Small-strain oscillatory shear measurements were performed in the frequency range from 0.05 to 50 Hz at several isotherms (between −15 and 100 °C, temperature range was dependent on the phase behavior of the sample, and step of the temperature was 5 °C) and frequency dependences of the storage G' and loss G'' moduli were measured at each temperature. The strain for those measurements was carried out within a linear viscoelastic regime; amplitude sweep (dependence of the modulus and strain on stress) was measured at several temperatures and frequencies to set the region of viscoelastic behavior. Using the frequency–temperature superposition data, the superimposed curves of reduced moduli $G'_p = G' \cdot b_T$, $G''_p = G'' \cdot b_T$ and loss tangent $\tan \delta_p = \tan \delta$ vs. reduced frequency $\omega \cdot a_T$ were obtained (where a_T is horizontal and b_T is vertical shift factor). The horizontal shift factor a_T was obtained from superposition of the loss tangent (for $\tan \delta$, no vertical shift is necessary).

III. RESULTS AND DISCUSSION

A. Thermal behavior

DSC data for thiol **MA**, neat PBD, and PBDs modified with thiol **MA** are summarized in Table I. Two peaks in the DSC curves occurred in the neat thiol.

TABLE I. DSC-data of the thiol **MA**, neat PBD, and PBDs grafted by thiol **MA** (R_c –degree of modification, estimated from elemental analysis). Heating and cooling rate was 10 °C/min.

Sample	R_c	Run	T_g °C	Δc_p J/g × °C	T_{m1} °C	ΔH J/g	T_{m2} °C	ΔH J/g	T_{m3} °C	ΔH J/g
PBD	0.00	H	−47.3	0.49	—	—	—	—	—	—
		C	−44.2	0.42	—	—	—	—	—	—
MA	—	H	—	—	88.0	90.7	110.0	2.9	—	—
		C	—	—	71.0	−83.1	108.0	−2.6	—	—
MA 0.2	0.21	H	−5.1	0.54	33.6	0.3	—	—	—	—
		C	−8.1	0.37	—	—	—	—	—	—
MA 0.4	0.30	H	7.2	0.56	39.1	1.1	—	—	—	—
		C	3.5	0.49	34.8	−0.7	—	—	—	—
MA 0.6	0.42	H	18.9	0.56	74.6	1.3	—	—	—	—
		C	19.0	0.77	73.1	−1.4	—	—	—	—
MA 0.8	0.57	H	^a	^a	35.7	5.2	63.1	−0.2	87.8	1.3
		C	^a	^a	27.5	^a	34.8	^a	86.9	−1.5
MA 1.0	0.55	H	^a	^a	62.5	−0.3	75.1	25.6	88.9	1.3
		C	^a	^a	47.0	−16.1	87.8	−1.7	—	—

^aNot determined.

During heating, the first peak at ~88.0 °C is responsible for a transition from a crystal-line phase to a mesophase, which resulted in a relatively high value of enthalpy (ΔH ~ 90.7 J/g). A POM image of this sample at 90 °C (heating regime 5 °C/min) is shown in Fig. 2(a). Inversion walls (grey field) with a Schlieren texture with disclinations of ± 0.5 (points with two arms) are typical for the presence of a nematic phase. The homogenous

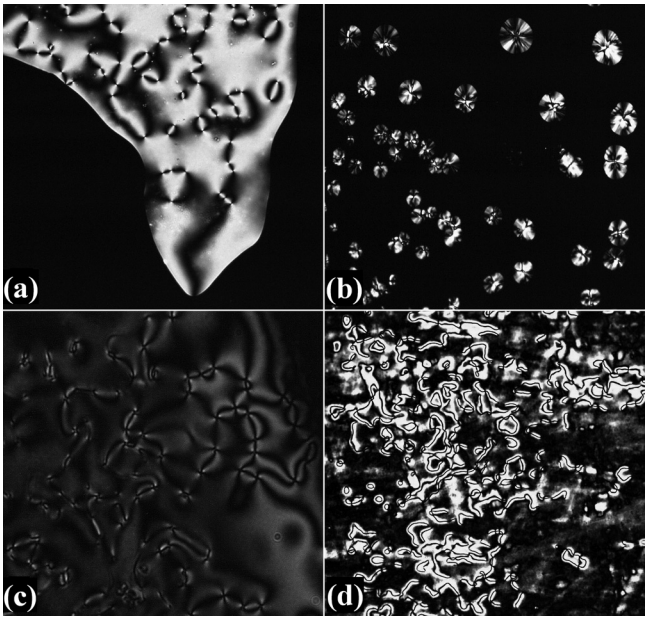


FIG. 2. POM images of thiol **MA** [(a) 90 °C, heating run] and related PBDs **MA 0.2** [(b) 25 °C, cooling run], **MA 0.6** [(c) 25 °C, cooling run], and **MA 0.8** [(d) 72 °C, cooling run]. Width of these pictures is 350 μ m.

black area corresponds to a place without sample. The nematic mesophase is stable up to 110.0 °C, which then begins to melt to an isotropic liquid ($\Delta H \sim 2.9$ J/g). Position of this peak was confirmed by a cooling run (~ 108 °C, $\Delta H \sim -2.6$ J/g), while the nematic-crystalline transition peak was slightly shifted (~ 71.0 °C, $\Delta H \sim 2.9$ J/g), probably due to a supercooling process at the cooling rate (10 °C/min).

After grafting of thiol **MA** onto double bonds of PBDs, related comblike polymers with varying amount of LC side chains (**MA 0.2** to **MA 1.0**) were obtained. DSC curves from cooling run for these polymers are shown in Fig. 3(a). Glass transition temperatures (T_g) of these structures and their Δc_p increase with increasing degree of modification, R_e (estimated from elemental analysis, see Table I), namely from -47.3 °C and 0.49 J/g \times °C (neat PBD) up to 18.9 °C and 0.56 J/g \times °C (**MA 0.6**). In polymers with $R_e > 0.42$, glass transition was not detectable on DSC upon measurement conditions, probably due to overlapping with a crystallization process. During heating, a small peak connected with melting of a mesophase to an isotropic liquid occurred in each polymer sample (Table I). Its temperature and enthalpy also increase with increasing amount of LC grafts, namely from 33.6 to 88.9 °C and from 0.3 to 1.3 J/g, respectively. Position of this peak was confirmed during cooling runs, with the exception of sample **MA 0.2**. As follows from our observation under polarizing microscope (rate 2 °C/min), when cooling **MA 0.2** from an isotropic state, a mesophase can be not easily induced in the whole area of this sample, probably due to lower content of mesogenic grafts (~ 21 mol. %). Figure 2(b) shows a place with nematic droplets of **MA 0.2** (25 °C, cooling run) in the black field indicating the presence of an isotropic liquid. The presence of nematics was observed in each polymer sample in the related temperature range above T_g . Namely, **MA 0.6** exhibits a very well-developed Schlieren texture with disclinations of both ± 0.5 and ± 1.0 [Fig. 2(c), at 25 °C, cooling run, 5 °C/min]. Disclination lines in **MA 0.8** can be seen as a typical threadlike texture [Fig. 2(d), 72 °C, cooling run, 5 °C/min]. Comparing the temperatures and enthalpies of the Iso/N transition in both original low-molecular thiol **MA** (~ 108 °C, -2.6 J/g) and PBD with the highest degree of modification (~ 88 °C, -1.7 J/g) and of the

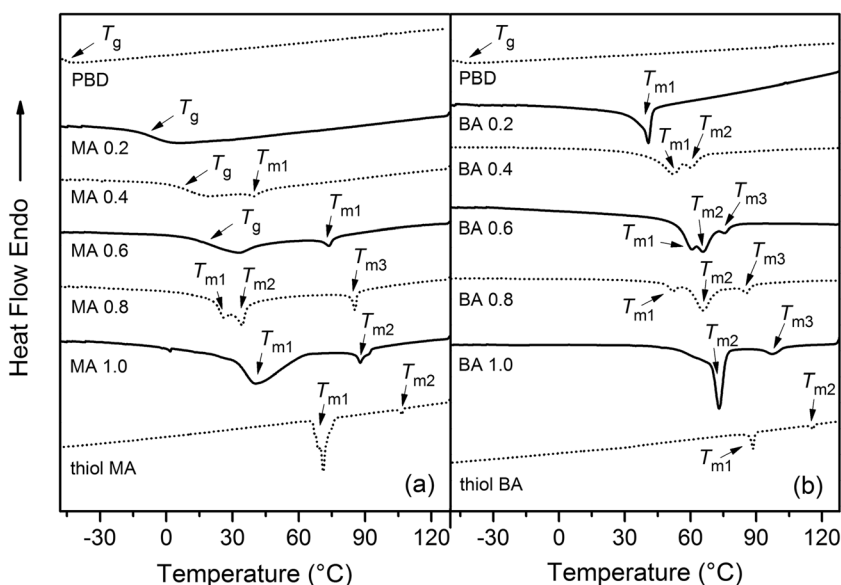


FIG. 3. DSC curves for neat PBD and PBDs grafted with thiol **MA** (a) and with thiol **BA** (b). Data collected from cooling run, rate 10 °C/min.

N/Iso transition in the thiol **MA** ($\sim 110^\circ\text{C}$, 2.9 J/g) and PBD **MA 1.0** ($\sim 89^\circ\text{C}$, 1.3 J/g), we can conclude that LC properties of the *para*-methoxyazobenzene are still influenced by the presence of the poly(butadiene) backbone.

Thermal behavior of the thiol **BA** (containing a butoxy group in the azobenzene *para*-position) differs significantly from the thiol **MA**. Table II summarizes results obtained by DSC for thiol **BA**. A sequence of several crystallization transitions, that was observed in a relatively broad temperature range ($70\text{--}93^\circ\text{C}$, heating run), resulted in a mesophase formation. An image of coexistence of this mesophase and a crystalline structure at 97°C (heating run, $5^\circ\text{C}/\text{min}$) is shown in Fig. 4(a). A black background indicating homeotropic alignment of the rodlike molecules and a Schlieren texture with four arms can be observed in both the nematic and smectic mesophase. However, Fig. 4(b) presents a different area of the sample where a rare marbled texture occurred, typical for the presence of nematics only. Hence, we concluded that thiol **BA** exhibits the presence of a nematic mesophase.

Strong tendencies for the thiol **BA** to form crystalline polymorphic structures have a significant impact on the phase and mesophase behavior of the related PBDs. Figure 3(b) presents DSC curves from cooling regimes for these polymers. Corresponding values of temperatures and enthalpies for all DSC transitions can be found in Table II. As follows from these data, no glass transition was detected, even in the case of the sample with the lowest content of grafts (**BA 0.2**, $\sim 22\text{ mol. \%}$). In this sample, only a semicrystalline structure was observed under POM. This corresponds to one broad peak on the cooling and heating curve. In all PBDs with higher amount of LC side-chains ($R_e \geq 0.30$), a small peak responsible for a mesophase formation occurred on cooling curves, moving to higher temperature values with increasing R_e . For **BA 0.4** and **BA 0.6**, this peak is still slightly overlapped by a crystallization peak, so it was not possible to determine enthalpy for each peak separately. Concluded from cooling curve DSC results, Fig. 3(b), temperature ranges, in which there is a mesophase, are broadened in accordance with increasing degree of modification of the sample. After grafting of the LC thiol on a polymer chain,

TABLE II. DSC-data of the thiol **BA**, neat PBD, and PBDs grafted by thiol **BA** (R_e – degree of modification, calculated from elemental analysis). Heating and cooling rate was $10^\circ\text{C}/\text{min}$.

Sample	R_e	Run	T_g $^\circ\text{C}$	Δc_p $\text{J/g} \times ^\circ\text{C}$	T_{m1} $^\circ\text{C}$	ΔH J/g	T_{m2} $^\circ\text{C}$	ΔH J/g	T_{m3} $^\circ\text{C}$	ΔH J/g	T_{m4} $^\circ\text{C}$	ΔH J/g
PBD	0.00	H	–47.3	0.49	–	–	–	–	–	–	–	–
		C	–44.2	0.42	–	–	–	–	–	–	–	–
BA	–	H	–	–	72.0	14.5	82.0	17.0	93.0	36.3	116.0	3.4
		C	–	–	89.0	–36.5	115.0	–3.5	–	–	–	–
BA 0.2	0.22	H	^a	^a	55.6	16.2	–	–	–	–	–	–
		C	^a	^a	40.5	–15.5	–	–	–	–	–	–
BA 0.4	0.30	H	^a	^a	60.4	5.8	73.2	5.9	–	–	–	–
		C	^a	^a	53.7	^a	62.8	^a	–	–	–	–
BA 0.6	0.36	H	^a	^a	69.8	14.1	91.9	3.5	98.1	0.7	–	–
		C	^a	^a	60.8	^a	66.1	^a	75.8	^a	–	–
BA 0.8	0.44	H	^a	^a	81.7	7.6	96.0	3.5	103.3	1.6	–	–
		C	^a	^a	53.0	–1.2	66.6	–9.1	87.2	–1.3	–	–
BA 1.0	0.52	H	^a	^a	91.2	21.1	106.2	0.6	–	–	–	–
		C	^a	^a	73.4	–22.1	98.2	–2.4	–	–	–	–

^aNot determined

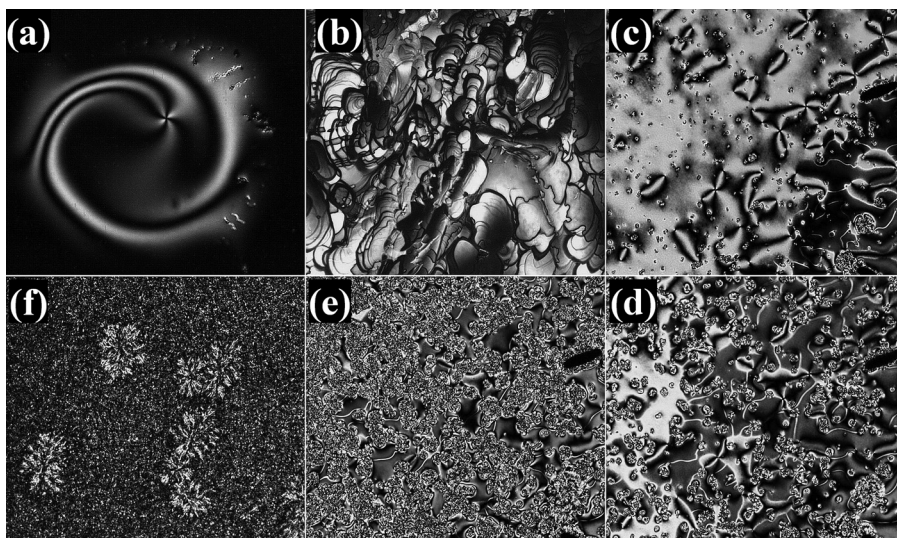


FIG. 4. POM images of thiol **BA** at 97 °C [(a) Schlieren texture, (b) marbled nematic texture; heating run] and N \rightarrow Cr transition of polymer **BA 1.0** [(c) 78 °C, (d) 76 °C, (e) 74 °C, (f) 60 °C, cooling run]. Width of pictures is 350 μ m.

the resulting comblike polymer should exhibit a mesophase at a maximum of the same level of arrangement as in the case of the neat thiol. Hence, we assumed the mesophase in polymers **BA 0.4–BA 1.0** is a nematic one. This fact was confirmed by polarizing microscope. An interesting sequence of images of mesophase/semicrystalline state transition was obtained for the polymer with the highest reached grafting density, sample **BA 1.0** [$R_e \sim 0.52$; Figs. 4(c)–4(f)]. In the nematic Schlieren texture with homogeneously aligned layers, in which the molecules are arranged parallel to a substrate layer, small crystallization centers start to appear [Fig. 4(c), 78 °C]. During continuous cooling, these centers with a spherulite structure became larger [Figs. 4(d) and 4(e)] and finally fill the entire sample space [Fig. 4(f), 60 °C]. The cooling rate of POM method was, in this case of PBD, with the highest degree of modification 5 °C/min, and the temperature values of the N/Cr transition are relatively comparable with those obtained from DSC-cooling (10 °C/min). When comparing DSC results obtained for the neat thiol **BA** and for the LC PBDs **BA 0.4–BA 1.0**, presence of the polymer chain has a significant influence on the thermal behavior of the *para*-butoxyazobenzene LC unit, i.e., temperature shift of the Iso/N transitions during cooling and heating run, narrower temperature intervals of the mesophase existence, and shifting of these intervals to lower values of temperatures. As also follows from the cooling curves for PBDs grafted with thiol **MA** [Fig. 3(a)] and with thiol **BA** [Fig. 3(b)], mesophase in LC PBDs **MA 0.4–MA 1.0** exists at lower temperatures and in broader temperature ranges than this in **BA 0.4–BA 1.0**.

B. Rheological testing

Temperature dependences of storage and loss moduli G' , G'' , and loss tangent, $\tan \delta$, of the selected PBDs grafted by thiol **MA** are shown in Fig. 5. During the cooling of PBDs **MA 0.2–0.6** from an isotropic state, a pronounced increase in G' is observed. The temperatures of Iso/N transition in **MA 0.4** and **MA 0.6** are slightly shifted to higher values in comparison with those found from DSC, due to higher cooling rate used in DSC measurement (10 °C/min). Continued cooling is accompanied with an increase in

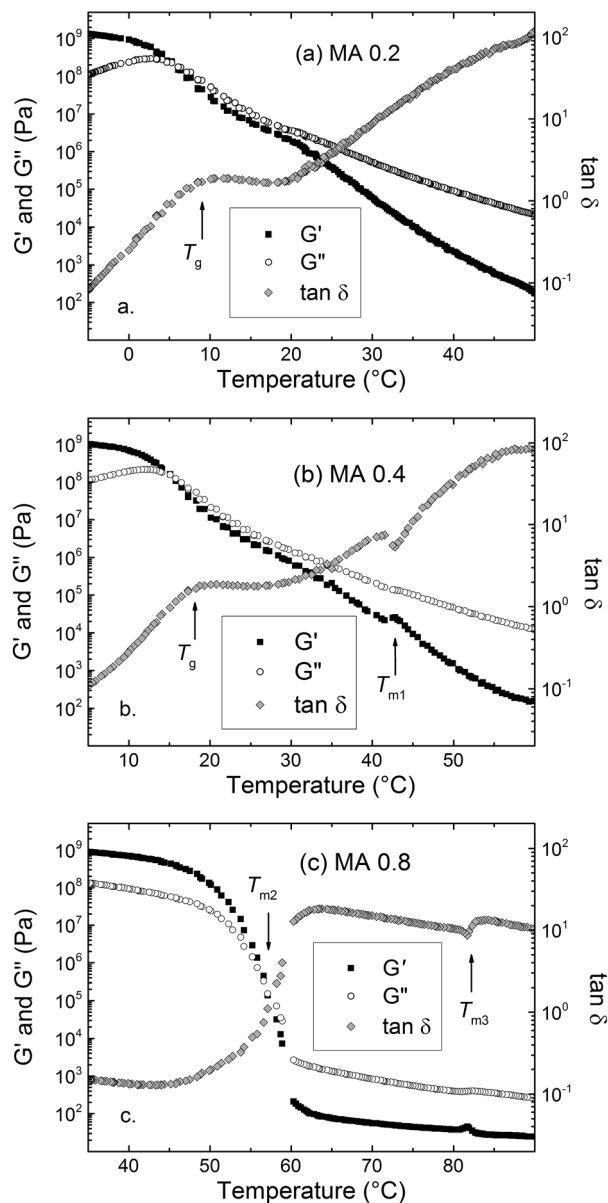


FIG. 5. Temperature dependences of moduli G' , G'' , and loss tangent $\tan \delta$ for LC PBDs **MA 0.2** (a), **MA 0.4** (b), and **MA 0.8** (c). Measured at $f = 1$ Hz, cooling rate $2^{\circ}\text{C}/\text{min}$.

G' , resulting finally in the glassy state with the highest values of the modulus corresponding to $\sim 10^9$ Pa. In PBD **MA 0.8** (and **MA 1.0**, not presented), transition from a semicrystalline phase to a glassy state results in a much sharper increase of G' in comparison to samples with lower grafting degree undergoing a direct nematic/glassy state transition.

As presented by Yu *et al.* (2007), the temperature regions for transitions in the material can be also detected from the much sensitive $\tan \delta$ vs. T plot. When cooling samples **MA 0.2–0.6** from an isotropic state, a nematic mesophase is formed. This results in a small drop in the loss tangent (marked as T_{m1} in Fig. 5). This drop was reproducibly

obtained during measurement with all types of plates. For temperatures below this local maximum, the material is purely nematic. With continuing cooling, the system is preparing for the glass transition resulting in the lowest values of loss tangent. A different behavior is present in samples with the highest content of mesogenic side chains, **MA 0.8–MA 1.0**. These materials exhibit semicrystalline phases, resulting in a loss of elastic properties. Crystallization of mesogens involved in the nematic LC arrangement is a very fast process in these PBDs. Due to the formation of growing crystals, the mobility of the polymer backbone segments is inhibited until a glassy state is reached.

Similar behavior was also expected in PBDs grafted by thiol **BA**. Figure 6 presents temperature dependencies of both moduli and loss tangent for PBDs **BA 0.4** (a) and **BA 0.8** (b). Common feature for these polymers is a Cr/glassy state transition exhibiting a very fast increase of both moduli and decrease of loss tangent as in cases of PBDs **MA 0.8–1.0**. During cooling of polymer **BA 0.4** from an isotropic state, moduli G' and G'' are slightly increasing. The Iso/Cr transition at ca. 70 °C is accompanied by a sharp increase of both moduli. Transition from a crystalline phase to a glassy state can be also clearly seen at ca. 54 °C (T_{m1}). After polymer reached the glassy state, value of G' corresponds to $\sim 10^9$ Pa. During cooling of the LC polymer **BA 0.8**, a formation of a semicrystalline structure from a mesophase was followed by a very sharp increase in G' and G'' . After

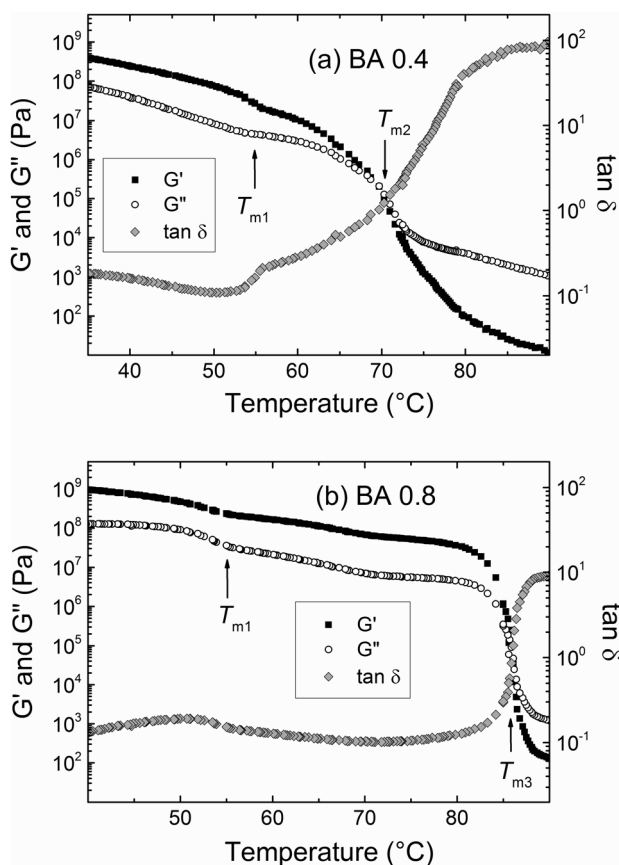


FIG. 6. Temperature dependencies of moduli G' , G'' , and loss tangent $\tan \delta$ for PBDs **BA 0.4** (a) and **BA 0.8** (b). Measured at $f = 1$ Hz, cooling rate 2 °C/min.

the sample reached the glassy state, elastic and viscous moduli remained almost constant ($\sim 10^9$ and 10^8 Pa, respectively).

Thermal behavior of a LC compound is strongly influenced by structure of the molecule. In this study, azobenzene mesogens possess an alkoxy-substituent (methoxy-, butoxy-) in the *para*-position of the aromatic core. The length of the alkoxy-substituent plays an important role in thermal behavior of the compound. Galewski *et al.* (1999) determined a strong tendency to a formation of several polymorphic crystalline structures in some low-molecular azobenzenes possessing butoxy-substituents. In a certain temperature interval, the crystalline/crystalline transition in polymorphic phases is thermodynamically more favorable than direct crystalline/nematic phase transition for molecules containing the butoxy-substituent.

The tendency to a formation of semicrystalline phases is preserved in the azobenzene with butoxy-substituent grafted on a flexible PBD backbone. We have observed that even small amount of **BA** units in side chains ($R_e \geq 0.22$) is sufficient for the formation of semicrystalline structures in the related polymer sample.

Different behavior was observed for methoxy-substituent on the azobenzene core. The neat mesogenic unit exhibits only one crystalline phase and the presence of a semicrystalline structure in PBDs grafted with MA is dependent on their degree of modification. Although a direct transition from a nematic phase to a glassy state was observed for PBDs with $R_e \leq 0.42$ during cooling, a semicrystalline phase occurred in these PBDs at higher degree of modification ($R_e > 0.42$).

The presence of the semicrystalline structure has a strong impact on the possibility to apply a temperature–frequency superposition for these LC polymer samples. For illustration, Fig. 7 presents the raw data of elastic modulus in dependence on frequency during isothermal measurements for two representative samples **MA 1.0** (a) and **BA 0.4** (b). A mesophase formation during cooling of polymer **MA 1.0** is accompanied by an increase of storage modulus. This fluent increase is disrupted when a semicrystalline oriented structure appeared in the sample [see Fig. 3(a)]. In the PBD **BA 0.4**, a mesophase exists in a relatively short temperature interval. As a consequence, an isotropic state/nematic transition is followed by a very fast nematic/semicrystalline transition. This process is connected with a rapid, discontinuous increase in storage modulus resulting in the impossibility to superimpose these points with only simple horizontal shift. From this angle of view, a superposition of mechanical functions G' , G'' , and $\tan \delta$ was applicable only for the samples undergoing direct nematic/glassy state transition.

During cooling from an isotropic state, a frequency–temperature superposition of dynamic mechanical functions has been successfully applied for the PDBs **MA 0.2–MA 0.6**. The horizontal shift factor, a_T , was obtained from the superposition of the loss tangent, $\tan \delta$. Using these a_T values, also G' and G'' dependencies could be superimposed. The temperature dependencies of the $\log a_T$ of the neat PBD and of the measured LC samples are shown in Fig. 8. They follow the Williams–Landel–Ferry (WLF) equation in the form [Sperling (2006)]

$$\log a_T = -c_1(T - T_{\text{ref}})/(c_2 + T - T_{\text{ref}}), \quad (1)$$

where T_{ref} is a reference temperature and c_1 , c_2 are constants (Table III). Reference temperature was chosen as 20 °C. This value of T satisfies the condition of WLF equation, $T_g \square T \square T_g + 100$, for all superimposed samples. In addition, the selection of the same T_{ref} for all samples enabled us a comparison of superimposed curves. The values of the vertical shift factor, b_T , were found to be close unity. From c_1 and c_2 , the fractional free volume at the reference temperature, f_0 , and the coefficient of thermal expansion of the

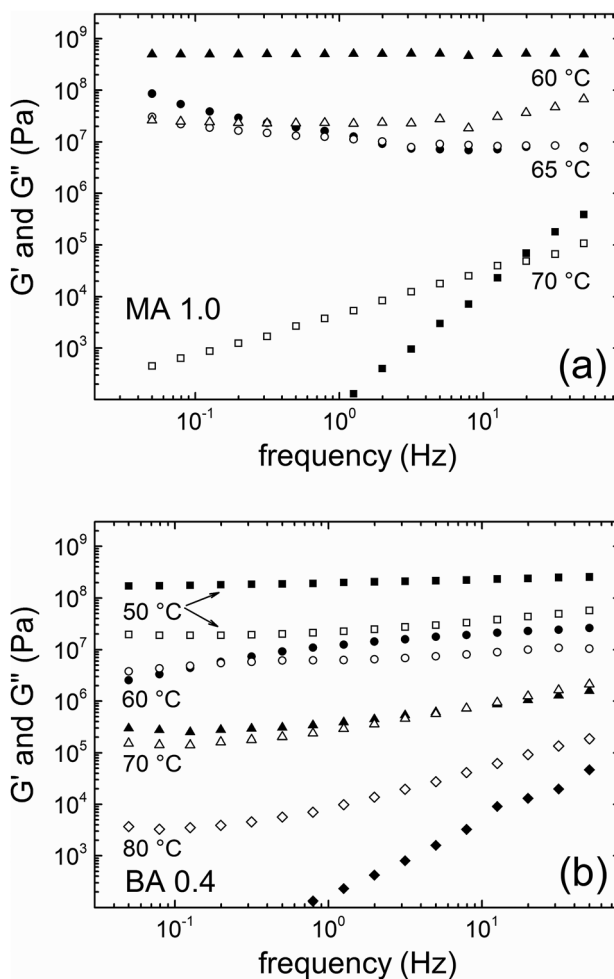


FIG. 7. Raw data for G' and G'' vs. frequency of the PBDs **MA 1.0** (a) and **BA 0.4** (b). Data collected during cooling regime, $T_{\text{ref}} = 20^\circ\text{C}$. Close symbols – G' , open symbols – G'' .

fractional free volume, α_f , were calculated ($f_0 = 1/2.3c_1$ and $\alpha_f = 1/2.3c_1c_2$, Table III). As expected, the free volume value was the highest in the case of the neat PBD ($f_0 = 0.111$), where the difference $T_{\text{ref}} - T_g$ is approximately 60°C . Values of f_0 calculated for other samples are getting closer to the universal value 0.025 as T_g is approaching T_{ref} . A thermal expansion coefficient, α_f , that is independent on the reference temperature, exhibited values very close to the universal one ($=4.8 \times 10^{-4} \text{ K}^{-1}$) in the case of the grafted PBDs. Nevertheless, values of both f_0 and α_f are within the range found for amorphous polymers, as follows from Sperling (2006).

The superimposed dependences of moduli G'_p , G''_p , and $\tan \delta$ on the reduced frequency $\omega \cdot a_T$ for the LC PBD samples modified with thiol **MA** are shown in Fig. 9. As the amount of grafted mesogenic chains increases, the dependences of moduli of the polymer (with respect to frequency) also increase. This results in a lower frequency extrapolation or longer predicted times. In the region of highest frequency (lowest temperature), G'_p of all the samples exhibits values above 10^9 Pa . The primary softening region causes, in all samples, a decrease in the superimposed moduli with decreasing frequency. Then, the grafted polymers are going through a glassy state/nematic transition which is

TABLE III. Constants of WLF equation and free volume parameters for the neat PBD and selected LC PBDs. T_{ref} was 20 °C.

Sample	R_e	c_1	c_2 (K)	f_0	$\alpha_f \times 10^4$ (K ⁻¹)
Neat PBD	0	3.9	94.6	0.111	11.8
MA 0.2	0.21	17.4	52.0	0.025	4.8
MA 0.4	0.30	18.2	35.4	0.024	6.7
MA 0.6	0.42	26.1	23.7	0.017	7.0

accompanied by a continuing decrease of both moduli. When the sample exhibits a presence of a nematic phase, the loss component, G_p'' , is higher than the elastic component, G_p' . At lowest frequencies, when polymers enter the flow region, the same trend of the moduli is observed. In this terminal region of the lowest frequencies, the slopes of dependencies of all mechanical functions vs. $\omega \cdot a_T$ that are typical for viscoelastic liquids [$G_p' \sim (\omega \cdot a_T)^2$; $G_p'' \sim (\omega \cdot a_T)^1$; $\tan \delta \sim (\omega \cdot a_T)^{-1}$] were found for the three grafted PBDs [Ferry (1980)].

It is interesting to note that the master curves cover fluently transitions both from a glassy state to a nematic mesophase and from the mesophase to an isotropic state. The similar phenomenon was observed previously in our research group [Jigounov *et al.* (2006)], when we applied the time–temperature superposition for cyanobiphenyl-containing mesogens grafted also on the poly(butadiene)-based polymer backbone. The master curves for both moduli and loss tangent were constructed over a broad frequency region comprising direct transition from a glassy state to a smectic A mesophase and melting of the mesophase to an isotropic liquid. According to our knowledge, only a few published works have been focused on the applicability of the time-temperature superposition for the side-chains liquid-crystalline polymers containing an azobenzene or a cyanobiphenyl mesogens. The polymer backbones were in these cases based on acrylates, methacrylates, or siloxanes [Colby and Gillmor (1993); Stein *et al.* (2001); Fourmaux-Demange *et al.* (1998); Yang and Chang (2002); Hotta and Terentjev (2003)]. However, the superposition worked mostly only during a mesophase/isotropic state

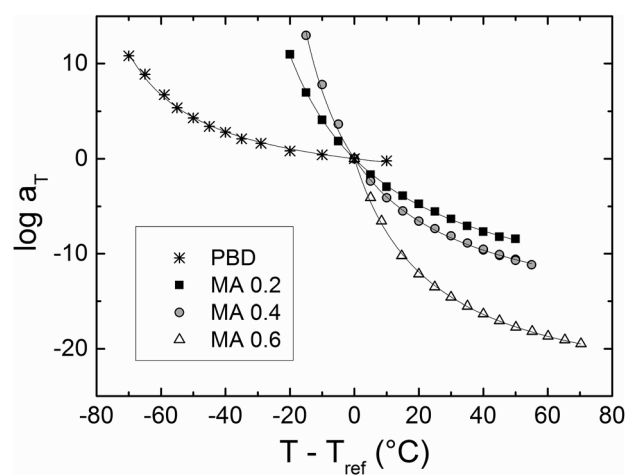


FIG. 8. Log a_T vs. temperature for the neat PBD (*) and PBDs MA 0.2 (■), MA 0.4 (●) and MA 0.6 (△). Solid lines follow the WLF-dependencies.

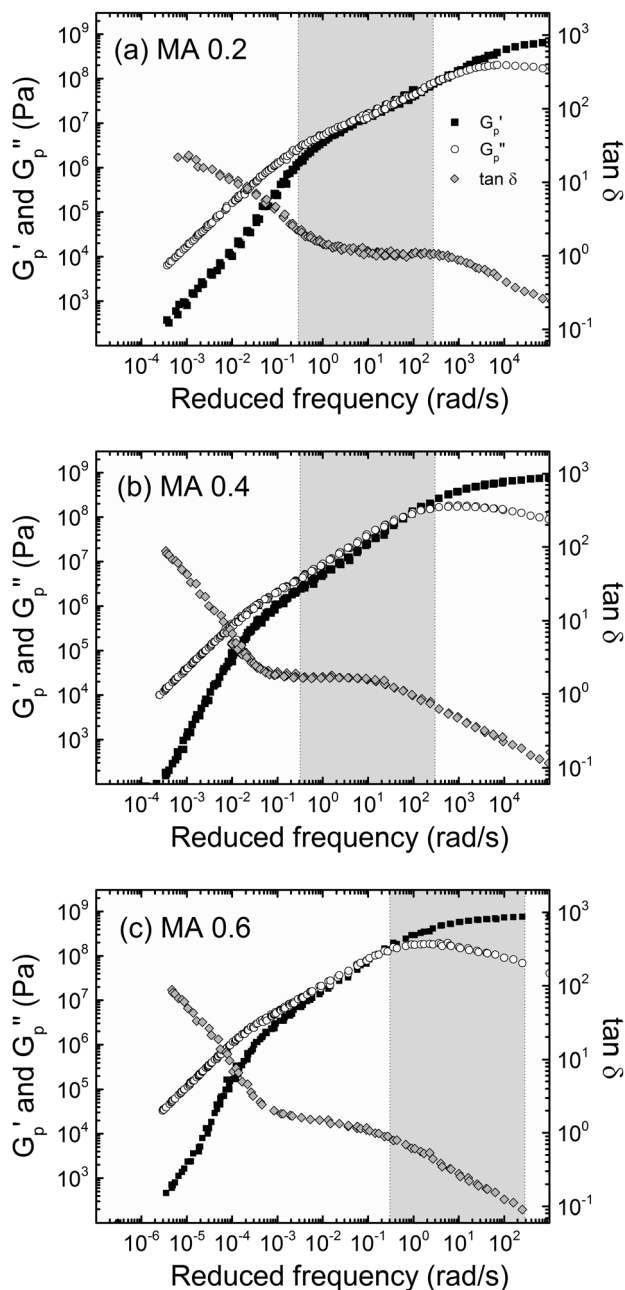


FIG. 9. Dependencies of the superimposed moduli G'_p , G''_p , and $\tan \delta$ on reduced frequency for the samples **MA 0.2** (a), **MA 0.4** (b), and **MA 0.6** (c). Data collected during cooling regime. Grey field presents the real frequency window (corresponding to $T_{ref} = 20^\circ\text{C}$).

transition. As a contrast, our unique synthetic route comprising grafting of the selected mesogens onto double bonds of poly(butadiene) enables to prepare LC polymers with very flexible polymer backbone. When the polymer sample exhibits a direct transition from a glassy state to a mesophase, a superposition during both the glass/mesophase and mesophase/isotropic transition is possible.

IV. CONCLUSIONS

The synthesized comblike LC PBD have been characterized by DSC and POM. T_g of these polymers increased with increasing degree of grafting. In samples with higher amount of grafts, glass transition was not detectable due to overlapping by a crystallization process. The polymers exhibit a presence of a nematic mesophase when containing at least 21 mol. % of thiol **MA** or 30 mol. % of thiol **BA** in side chains. Dynamic mechanical measurement was used to investigate mechanical properties of the samples. A superposition of mechanical functions (storage and loss moduli and loss tangent) was successfully constructed for neat PBD and for LC polymer samples with direct nematic/glassy state transitions.

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