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Synthesis and thermal behavior of telechelic poly(butadiene)diols with azobenzene-based liquid-crystalline units in side chains

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Abstract Mesogenic thiols with azobenzene as a rigid part and with various substituent (H-, methoxy-, butoxy- or octyloxy-) in *para*-position of azobenzene ring were synthesized by multi-step syntheses. The thiols were grafted onto double bonds of telechelic poly(butadiene)diol ($M_n \sim 2{,}400$, functionality $f_n = 2$, 60 mol.% of 1,2-butadiene units) via radical addition in the presence of 2,2′-azobis(2-methylpropionitrile) (AIBN). Initial mole ratio of thiol/double bonds varied in the range of 0.2–1.0. Influence of the azobenzene substituent on the extent of modification reaction was estimated using elemental analysis, size-exclusion chromatography and ^{1}H NMR spectroscopy. The substituent on mesogen plays also an important role in thermal behavior of both the thiols and the obtained comb-like polymers, as determined by differential scanning calorimetry and polarizing optical microscopy.

Keywords Azobenzene mesogens · Radical addition · Poly(butadiene)diols · Liquid-crystalline polymers · Thermal behavior

Introduction

Liquid-crystalline (LC) polymers are attractive materials. Due to their properties they can be used in photonic, ferroelectric and antiferroelectric applications or in non-linear optics [1–4]. Introduction of azobenzene into polymer side chains usually leads to the preparation of such polymers [5–7]. Azobenzene-based

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mesogens belong to an important class of photochromic materials, distinguished by birefringence and optical dichroism based on *cis*/*trans* isomerization of azochromophore group [8, 10, 11]. Many liquid-crystalline azobenzene-based side-chain polymers have been already synthesized and studied; however, their main chains were usually based on poly(acrylate), poly(methacrylate) or poly(siloxane) [9–11].

In this work, we have synthesized four rod-like azobenzene-based mesogens with various substituent (H-, methoxy-, butoxy- or octyloxy-) and pentamethylene spacer containing thiol end group, both in *para*-positions of the azobenzene ring. To prepare the novel type of polymers with LC-units in side chains, we have selected telechelic polybutadiene-diol (commercially available as Krasol LBH 3 000, $M_n \sim 2{,}400$, declared functionality $f_n = 2$) as the main polymer backbone. Main reasons of the selection of this polymer are its flexibility (important for possible LC-arrangement of the mesogens bound in side chains [6]) and content of approximately 60 mol.% of 1,2-butadiene units that can easily undergo a convenient modification reaction. Moreover, the polymer chain contains hydroxyl groups at the ends; thus, it can be employed in further reactions leading, i.e. to polyurethanes or block copolymers with LC-properties. As mentioned above, all the synthesized mesogens contain thiol group; by radical addition of the thiol on the double bonds of poly(butadiene)diol, four sets of grafted telechelic poly(butadiene)diols with different degrees of modification have been prepared.

The composition and the final structure of both the low-molecular and the comb-like polymer analogues have been investigated by elemental analysis, size-exclusion chromatography (SEC) and ^{1}H NMR spectroscopy. Thermal behavior was estimated from differential scanning calorimetry (DSC). The LC-mesophases were determined by small-angle X-ray scattering (SAXS) and polarizing optical microscopy (POM).

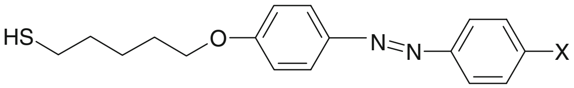
Synthesis and characterization

Materials

Aniline (b.p. 184 °C/101.3 kPa, Fluka), 1,5-dibromopentane (b.p. 110 °C/2.0 kPa, Fluka), *p*-anisidine (b.p. 241 °C/101.3 kPa, Fluka) were distilled prior to use. Thiourea (m.p. 170–176 °C, Fluka) and *n*-butanol (b.p. 116–118 °C/101.3 kPa, Fluka) were used as received. Telechelic poly(butadiene)diol (Krasol LBH 3 000, Sartomer; the polymer contains ~60 mol.% of 1,2-, ~25 mol.% of *trans*-1,4- and ~15 mol.% of *cis*-1,4-butadiene units) was dissolved in *t*-butyl methyl ether, precipitated with methanol several times to remove inhibitor and dried under reduced pressure. 2,2′-Azobis(2-methylpropionitrile) (AIBN, m.p. 102–104 °C, Fluka) was recrystallized from methanol. All the solvents used were of analytical grade.

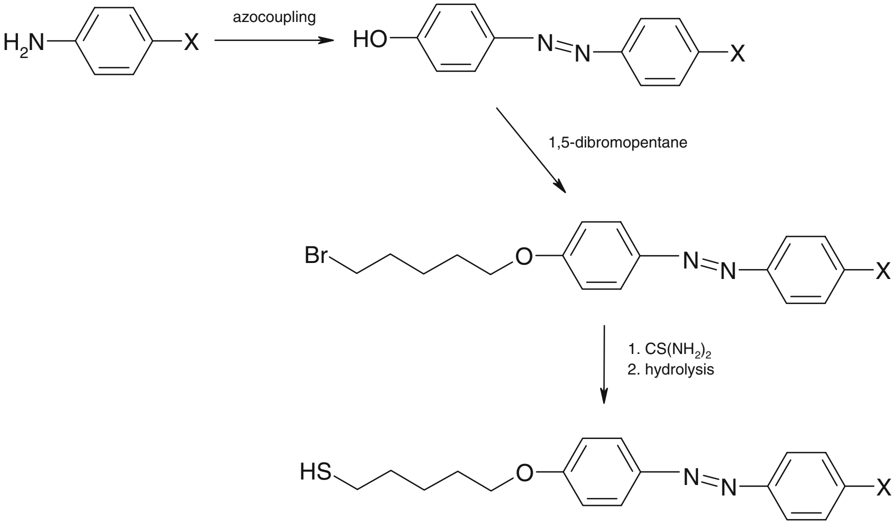
Synthesis of thiols

The following thiols A, MA, BA and OA were synthesized:

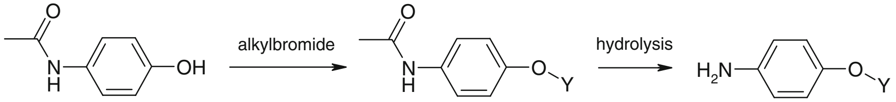


X = -H (A)
-OCH_3 (MA)
-$O(CH_2)_3CH_3$ (BA)
-$O(CH_2)_7CH_3$ (OA)

The thiols containing both the mesogenic azo-group and the pentane-1,5-diyl spacer group were prepared by a multi-step synthesis (Scheme 1). Scheme 2 illustrates the preparation of reagents 4-butyloxyaniline and 4-octyloxyaniline for the synthesis of thiols BA and OA, respectively.



Scheme 1 General scheme of the synthesis of thiols A, MA, BA and OA. Substituent X = –H, –OCH_3, –$O(CH_2)_3$–CH_3, –$O(CH_2)_7$–CH_3



Scheme 2 Preparation of 4-(butyloxy)aniline and 4-(octyloxy)aniline. Y = –$(CH_2)_3$–CH_3 or –$(CH_2)_7$–CH_3

Synthesis of 5-(4-[phenylazo]phenoxy)pentane-1-thiol (A)

Synthesis of 4-(hydroxy)azobenzene (1) A mixture of 9.31 g (0.1 mol) of aniline and 45 ml of 18 wt.% HCl was heated until complete amine dissolution. The obtained solution I was cooled and kept at 0–5 °C. At this temperature, 10.1 g (0.146 mol) of $NaNO_2$ in 58 ml of water was added dropwise to the solution I. Then, at 0–5 °C, the clear solution of diazonium salt was added dropwise to a solution of 20.5 g (0.218 mol) of phenol and 17.4 g (0.435 mol) of NaOH in 215 ml of water. The reaction temperature was maintained below 5 °C. Finally, the reaction mixture was neutralised with HCl. The precipitate was filtered off, washed with ice water and dried. The crude product was recrystallized from hexane, m.p. 155–156 °C. Yield: 14.05 g (70.9%).

Synthesis of 4-[(5-bromopentyl)oxy]azobenzene (2) 25 g (0.126 mol) of (**1**) was dissolved in 600 ml of dry ethanol, 9.79 g (0.17 mol) of KOH and 250 g (1.08 mol) of 1,5-dibromopentane were added and reaction mixture was heated to 75 °C for 6 h. Then the reaction mixture was cooled to room temperature and the solid was filtered off. The filtrate was concentrated in vacuum to crystallization. The precipitated crystals were filtered off and recrystallized from ethanol/heptane (1/9), m.p. 114–115.5 °C. Yield: 41.47 g (94.5%).

Synthesis of 5-(4-[phenyl]azophenoxy)pentane-1-thiol (3) A mixture of 34.82 g (0.1 mol) of compound (**2**) and 8.37 g (0.11 mol) of thiourea in 400 ml of absolute ethanol was heated at 80 °C for 20 h. Then the reaction mixture was cooled to room temperature and concentrated in a rotavapor. The obtained thiuronium salt was filtered off and recrystallized from absolute ethanol; m.p. 186–187 °C. Yield 41.34 g (97.2%). Then, 28.91 g (68 mmol) of thiuronium salt was hydrolysed by refluxing with a solution of 5.18 g (90 mmol) of KOH in a mixture of 350 ml of ethanol and 250 ml of water under nitrogen for 7 h. After cooling to room temperature, the reaction mixture was acidified with acetic acid to neutral reaction. Ethanol was then evaporated in vacuum and the crude product was extracted with chloroform. The chloroform solution was extracted with water and dried over anhydrous calcium chloride. The solvent was evaporated in a rotavapor to give the crude thiol A that was recrystallized from heptane; m.p. 67–68 °C. Yield 18.64 g (91%).

Synthesis of 5-(4-{[4′-(methoxy)phenyl]azo}phenoxy)pentane-1-thiol (MA)

Synthesis of 4-hydroxy-4′-(methoxy)azobenzene (4) The preparation was carried out similarly to the synthesis of (**1**), with *p*-anisidine instead of aniline. M.p. of the product: 139–141 °C. Yield: 16.18 g (70.9%).

Synthesis of 4-[(5-bromopentyl)oxy]-4′-(methoxy)azobenzene (5) 27.85 g (0.122 mol) of compound (**4**), 40 g K_2CO_3 and 241.2 g (1.048 mol) of 1,5-dibromopentane were dispersed in 560 ml of dry acetone and heated under reflux for 48 h. Then the reaction mixture was cooled to room temperature and the solid was filtered off. The filtrate was concentrated in vacuum to crystallization. The precipitated crystals were filtered off and recrystallized from ethanol/heptane (1/9), m.p. 104–105 °C. Yield: 27.61 g (94.5%).

Synthesis of 5-(4-{[4′-(methoxy)phenyl]azo}phenoxy)pentane-1-thiol (6) Similarly to the synthesis of (**3**); m.p. of the thiuronium salt was 204.5–205.5 °C, yield: 27.05 g (90%). M.p. of the final thiol: 87–88 °C. Yield 12.77 g (88%).

Synthesis of 5-(4-{[4′-(butyloxy)phenyl]azo}phenoxy)pentane-1-thiol (BA)

Synthesis of butylbromide (7) 59.5 g (0.5 mol) of kalium bromide was dissolved in 60 ml of water and 44.47 g (0.6 mol) of *n*-butanol was added. While cooling the reaction mixture on an ice bath, 60 ml of conc. sulphuric acid was added in small portions under stirring. Then the mixture was heated under reflux for 2 h. The prepared crude butylbromide was distilled off and purified by shaking in separatory funnel subsequently with 50 ml of water, 25 ml of cooled conc. sulphuric acid, water, 30 ml of saturated solution of sodium carbonate and again with water. After drying over calcium chloride, butylbromide was finally purified by distillation; b.p. 99–102 °C, $n_D = 1.4378$. Yield: 65.8 g (80%).

Synthesis of 4-(butyloxy)aniline (8) (Scheme 2): 50 g (0.33 mol) of 4-(acetamido)phenol was dissolved in a solution containing 18.5 g (0.33 mol) KOH and 400 ml of aqueous ethanol (1:1), then 50 g (0.36 mol) of (**7**) in 400 ml of ethanol was added and temperature was raised to 75 °C. Stirring continued for 48 h. The reaction mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. The precipitate was filtered off and washed with an aqueous solution of NaOH (5 wt.%) and water. The crude *N*-[(4-(butyloxy)phenyl]acetamide (m.p. 108–110 °C) was heated with 267 ml of 20 wt.% sulfuric acid at 95 °C for 90 min. Then the reaction mixture was cooled to room temperature, the amine salt was filtered off and repeatedly washed with water. The salt was suspended in 500 ml of water at 80 °C, a solution of 10 g of NaOH in 20 ml of water and 200 ml of toluene were added and the reaction mixture was heated under reflux for 8 h. After cooling to room temperature, the toluene layer was separated and water layer was extracted three times with 50 ml of toluene. The toluene solution was dried over NaOH and molecular sieves. The filtrate was concentrated in a rotavapor and the residual oil was purified by distillation; b.p. 80–80.5 °C/6.7 Pa. Yield: 44.7 g (82.5%).

Synthesis of 4-hydroxy-4′-(butyloxy)azobenzene (9) The preparation was carried out similarly to the synthesis of (**1**), with 16.52 g (0.1 mol) g of (**8**) instead of aniline. M.p. of the product: 103–104 °C. Yield: 16.54 g (61.2%).

Synthesis of 4-[(5-bromopentyl)oxy]-4′-(butyloxy)azobenzene (10) Similarly to the synthesis of (**5**). M.p. of the obtained product: 114–115.5 °C. Yield: 12.94 g (95%).

Synthesis of 5-(4-{[4′-(butyloxy)phenyl]azo}phenoxy)pentane-1-thiol (11) Similarly to the synthesis of (**3**); m.p. of the thiuronium salt was 185–186.2 °C, yield: 14.78 g (96.5%). M.p. of the final thiol: 97–98 °C, yield: 9.42 g (85%).

Synthesis of 5-(4-{[4′-(butyloxy)phenyl]azo}phenoxy)pentane-1-thiol (OA)

Details of synthesis of the thiol OA can be found in Ref. [12].

Preparation of comb-like PBDs

For the preparation of the grafted PDBs, telechelic poly(butadiene)diol (commercially available as Krasol LBH 3 000, $M_n \sim 2{,}400$, 40 mol.% of 1,4-butadiene units, declared functionality $f_n = 2$) was dissolved in dry toluene (a 1 mol/l solution). Then, a certain amount of thiol (A, MA, BA or OA) was added; the initial mole ratio of SH/PB double bonds varied within the range of 0.2–1.0 for each type of the thiol used. The grafting reactions were carried out in the presence of AIBN (mole ratio of AIBN/SH = 5×10^{-2}) under nitrogen atmosphere at 60 °C. After 48 h, the solvent was evaporated, polymer was precipitated in methanol, dried under reduced pressure at 40 °C, several times washed with methanol and dried again.

Characterization of the PBDs

The composition and structure of the synthesized thiols (A, MA, BA and OA) were confirmed by elemental analysis and ^{1}H NMR spectroscopy. After addition and purification reactions, the experimental degree of modification of the poly(butadiene)diols, R_m, was determined from elemental analysis (R_E) using weight fractions of sulphur bound in LCPBDs. The ^{1}H NMR and ^{13}C NMR spectroscopy (300.1 and 75 MHz, respectively, 60 °C) were also used for its determination (R_{NMR}). Using size-exclusion chromatography (SEC) equipment (modular LC system with refractive index detection, column 30 × 8 SDV 10000, PS-standards, THF as eluent, measurements carried out at ambient temperature), number- and weight-average molecular weights were evaluated and the extent of grafting reactions was determined (R_{SEC}).

Thermal properties of the samples were measured on a PerkinElmer differential scanning calorimeter DSC-7e. The data from cooling and subsequent heating at a rate of 10 °C/min were collected. Textures of crystalline and liquid-crystalline phases were observed by a polarizing optical microscope (Nikon Eclipse 80i); the heating/cooling rate was 5 °C/min.

Results and discussion

Modification of PBDs

Poly(butadiene)diol (PBD) was grafted with the synthesized thiols (A, MA, BA and OA); initial mole ratio of SH/double bonds varied in the range from 0.2 to 1.0. Figure 1 shows the dependence of number-average molecular weights (M_n) on the initial mole ratio of thiol/double bonds (R_0) for all the prepared comb-like PBDs. This graph demonstrates a desired trend of increasing relative values of molecular weights in all sample sets with increasing R_0.

The amount of grafts in the prepared comb-like polymers was estimated from elemental analysis (R_E) and from ^{1}H NMR (R_{NMR}). For PBDs modified with thiol MA and OA, the comparison of results obtained from these methods is shown in Fig. 2. As expected, the dependences indicate a growing tendency with increasing

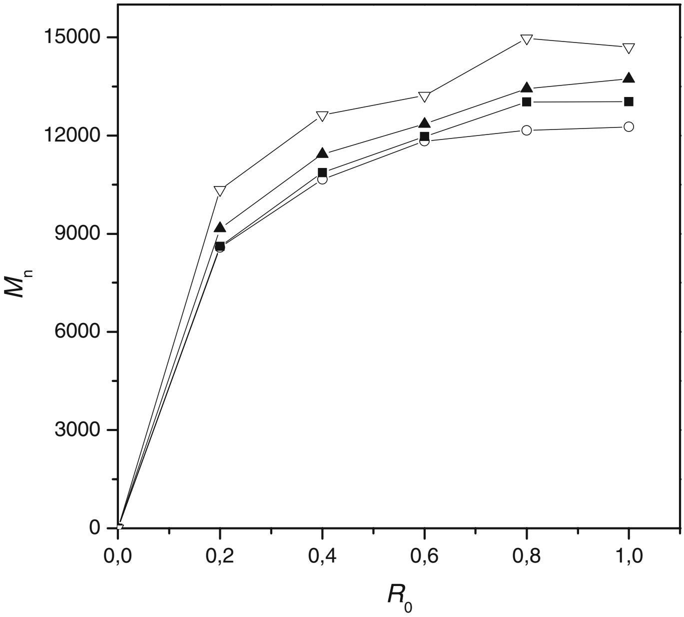


Fig. 1 Number-average molecular weights (M_n, from SEC) versus initial mole ratio of thiol/double bonds (R_0) for PBDs grafted with thiol A (*open circle*), MA (*filled square*), BA (*filled triangle*), OA (*inverted open triangle*)

mole ratio of SH/double bonds in the feed. From Fig. 2 it also follows that the extent of modification reactions for PBDs is not strongly influenced by the individual substituent (methoxy-, octyloxy-) in *para*-position of azobenzene-based grafting unit. Probably due to steric hindrances that prevent the addition reactions of the large thiol-molecules onto double bonds incorporated in polymer main chain containing ~60 mol.% of pendant vinyl units, the highest calculated R_m reached up 80 mol.% for all sets.

Thermal behavior

Thiols

DSC-transitions of thiols are shown in Table 1. In the case of the first sample (thiol A, substituent X = H), no mesophases were detected; on cooling and subsequent heating, only the formation (53 °C) of a crystalline phase and its melting (65 °C), respectively, were observed. The introduction of methoxy-group into thiol structure (sample MA) led to an increase of temperature of crystalline phase melting (88 °C) and shifted strongly enthalpies to higher values. Moreover, one mesophase/isotropic state transition occurred at 110 °C on heating run with corresponding $\Delta H \sim 2.9$ J/g. The position of this peak was confirmed by cooling run, giving 108 °C and $\Delta H \sim -2.6$ J/g.

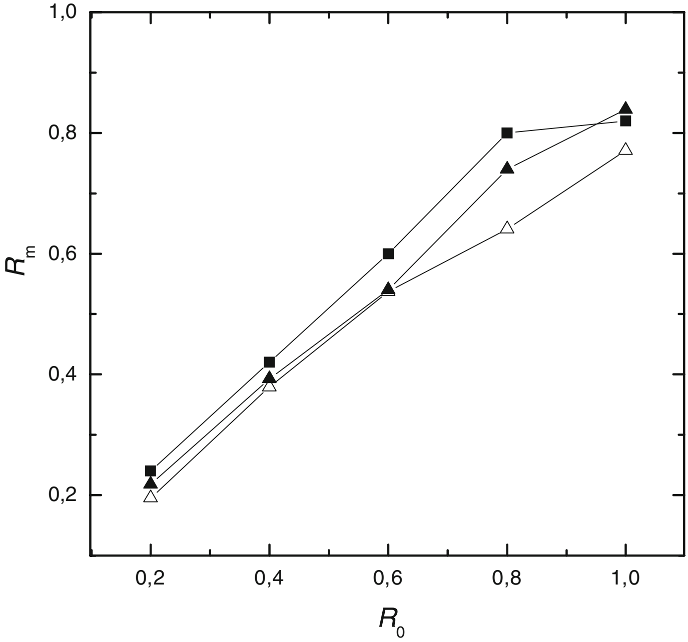


Fig. 2 Dependence of degree of modification (R_m) of LCPBDs grafted with thiol MA and OA on the initial mole ratio of SH/double bonds (R_0); R_m determined from ^{1}H NMR (*filled square* MA, *filled triangle* OA) and elemental analysis (*open triangle* OA)

Table 1 DSC-data of the synthesized thiols

Thiol	Run	T_{m1}		T_{m2}		T_{m3}		T_{m4}		T_{m5}	
		°C	ΔH (J/g)	°C	ΔH (J/g)	°C	ΔH (J/g)	°C	ΔH (J/g)	°C	ΔH (J/g)
A	H	65.1	24.4								
	C	53.0	−21.2								
MA	H			88.0	90.7					110.0	2.9
	C			71.0	−83.1					108.0	−2.6
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
OA	H			83.0	68.4			102.0	3.5	116.0	3.8
	C			60.0	−61.9			101.0	−2.9	114.0	−4.0

The most complex thermal behavior was observed in the sample BA (X = butoxy). The formation and subsequent partial melting of various crystallites arrangement appeared only on heating (T_{m1} and T_{m2}); then the final crystalline phase melting followed at 93.0 °C (T_{m3}). Compounds of similar architecture, namely from the 4-butoxy-4′-alkoxyazobenzenes family, show a crystalline polymorphism; the detailed description of this phenomena can be found in Ref. [13]. One liquid-crystalline/isotropic state transition occurred; temperature and enthalpy of the mesophase melting (116 °C and ΔH ~ 3.4 J/g, respectively) slightly increased in comparison with those in the previous sample MA (110 °C and ΔH ~ 2.9 J/g). On subsequent cooling, the formation of a LC-phase is observable (~115 °C) and is followed by a crystallization peak (~89 °C, ΔH ~ −36.5 J/g). Determination of the types of mesophases is under study.

Thiol OA with the longest octyloxy-substituent exhibits a richer LC-behavior. On cooling, the formation of the first mesophase took place at 114 °C (ΔH ~ −4.0 J/g), the next LC-transition was at 101 °C (ΔH ~ −2.9 J/g). The LC-states were evaluated as SmA and SmC [14]. Subsequently, during the cooling, crystallization of the thiol started at 60 °C. As expected, the values of enthalpies of all mentioned smectic/isotropic transitions were much lower than those corresponding to crystalline phase melting.

Liquid-crystalline PBDs

DSC results obtained for the neat PBD and LCPBDs grafted with thiol MA are summarized in Table 2. The data indicate that only the former PBD shows a simple amorphous thermal behavior with one glass transition. Due to the introduction of mesogens having a more rigid nature than butadiene units, the values of detected T_g and related Δc_p increase with increasing amount of grafts in the polymer chain, namely from −47.3 (PBD) up to 18.9 °C (MA 0.6, R_{NMR} ~ 60 mol.%) and from 0.49 to 0.56 J/gK, respectively.

Temperature of the LC-transition also increased with the increasing degree of modification (samples MA 0.2–1.0). Considering that the mesophase/isotropic state transition occurs in the neat thiol MA at temperature ~110 °C (Table 1), it can be noted that the formation of the mesophase of the mesogen molecule bound on the poly(butadiene) chain is still strongly influenced by the presence of the flexible

Table 2 Degree of modification (R_{NMR}) and DSC results of the neat PBD and related LCPBDs, grafted by thiol MA

Sample	$R_{NMR} \times 100$	Run	T_g		T_{m1}		T_{m2}		T_{m3}	
			°C	c_p (J/g)	°C	ΔH (J/g)	°C	ΔH (J/g)	°C	ΔH (J/g)
PBD	0	H	−47.3	0.49						
		C	−44.2	0.42						
MA 0.2	24	H	−5.1	0.54					33.6	0.30
		C	−8.1	0.37						
MA 0.4	42	H	7.2	0.56					39.1	1.07
		C	3.5	0.49					34.8	−0.71
MA 0.6	60	H	18.9	0.56					74.6	1.30
		C	19.0	0.77					73.1	−1.35
MA 0.8	80	H			35.7	5.19	63.1	−0.21	87.8	1.25
		C			34.8	−7.85			86.9	−1.45
MA 1.0	82	H			62.5	−0.28	75.1	25.59	88.9	1.33
		C			47.0	−16.08			87.8	−1.71

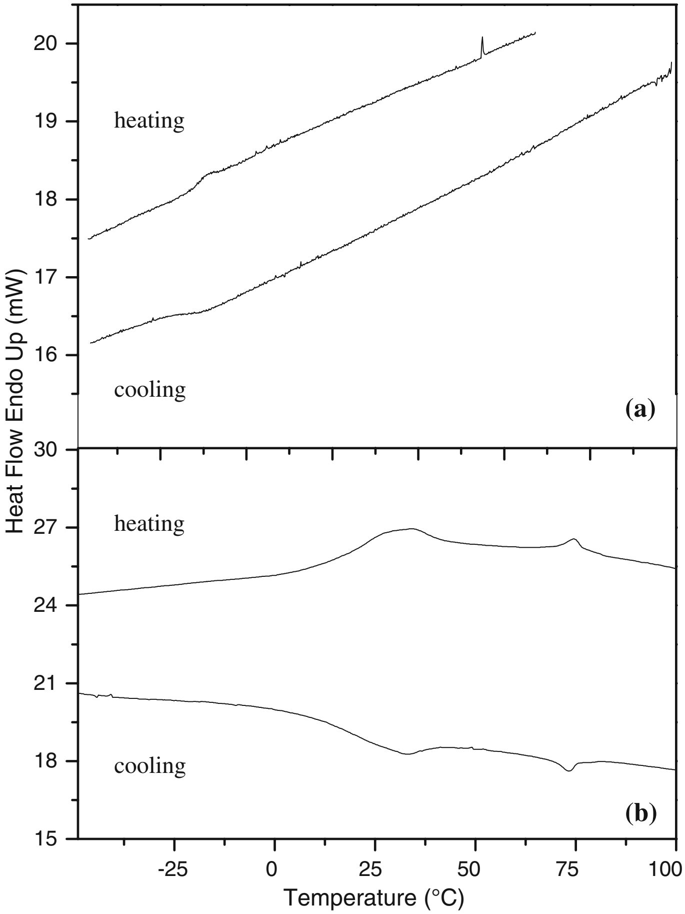


Fig. 3 DSC traces of the neat PBD (**a**) and the grafted MA 0.6 ($R_{\mathrm{NMR}} \sim 60$ mol.%) (**b**). Cooling and heating rate: 10 °C/min

polymer backbone, even in the sample with the highest amount of grafts (MA 1.0; $T_{\mathrm{m3}} \sim 89$ °C).

An example of DSC traces of both the original PBD and one of the grafted LCPBDs (MA 0.6, $R_{\mathrm{NMR}} \sim 60$ mol.%) is shown in Fig. 3. On heating/cooling the sample MA 0.6, one small peak corresponding to a mesophase melting/formation was detected ($\sim$74 °C).

Figure 4 shows the dependences of the temperature of detected glass and liquid-crystalline transitions (the data used were collected from DSC-thermograms, heating run) on both the degree of modification and structure of the grafted thiol (A, MA and BA). As expected, no LC-behavior of the PBDs grafted with thiol A occurred. In corresponding addition reactions, the T_g-values of these PBDs slightly increased with the increasing amount of the thiol in the feed. The introduction of methoxy- (resp. butoxy-) substituent in *para*-position of

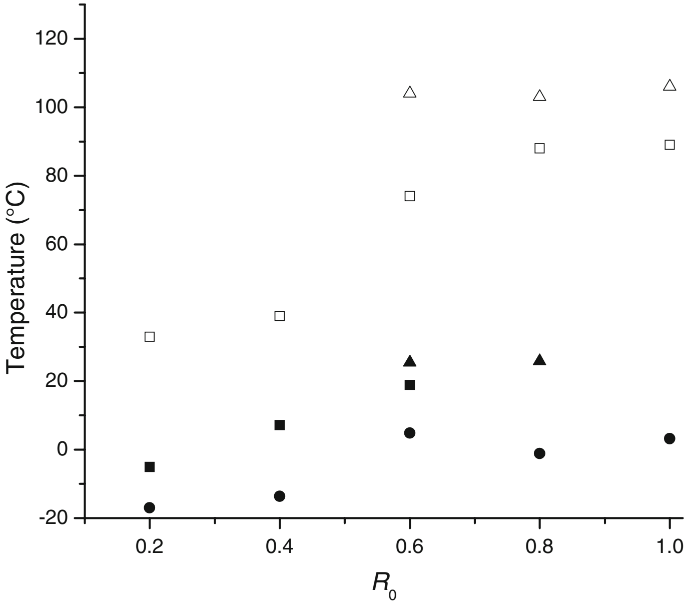


Fig. 4 Dependence of temperature of glass transition (T_g) and mesophase/isotropic state transition (T_{LC}) of PBDs on initial mole ratio of thiol/double bonds (R_0) in grafting reaction. Modifying thiols: *filled circle* A, *filled square* MA, *filled triangle* BA (relate to T_g), *open square* MA, *open triangle* BA (relate to T_{LC})

azobenzene in side-chain units shifted glass transition temperatures of related LCPBDs to higher values in comparison with those of LCPBDs grafted with thiol A. Similarly to the polymer samples grafted by thiol MA, temperature of LC-transition in a polymer containing the highest reached amount of 4′-butoxy-azobenzene mesogen units in side chains is lower than that in the neat thiol BA (Table 1, ~116 °C). The investigation of the mesophase types of the PBDs grafted by thiols MA and BA is under way.

Conclusions

Mesogen thiols containing azobenzene as a rigid part and a pentane-1,5-diyl spacer were synthesized and grafted on double bonds of telechelic poly(butadiene)diol with varying initial mole ratio of thiol/double bonds in the feed. It was shown that the degree of modification of such comb-like polymers increased with the increasing thiol amount in the feed in grafting reaction; at the same time, it was practically independent on the mesogen substituent (H-, methoxy-, butoxy- or octyloxy-). As follows from DSC-measurements, thiols with methoxy- or butoxy- substituent showed one LC-transition, whereas those with octyloxy-substituent exhibited two LC-transitions. The influence of the type of substituent in polymer grafts on T_g and

T_{LC} was observed. A more detailed study of the mesophases using SAXS and polarizing optical microscopy will be presented in the near future.

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