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Synthesis and Solution Properties of Polymethacrylates with Alicyclic Side Groups

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ABSTRACT: The influence of alicyclic side groups on the unperturbed chain dimensions of polymethacrylates is reported. Cyclobutyl, cyclopentyl, cyclooctyl, and cyclododecyl side groups resulted in characteristic ratios respectively of 10.0, 11.2, 12.1, and 14.2. These findings indicate that an increase in the size of the alicyclic side group leads to a concomitant enhancement in C_∞. The same trend was previously noted for poly(n-alkyl methacrylates). For alicyclic side groups C_∞ is larger than for the corresponding poly(n-alkyl methacrylate). These differences are attributed to the diminished flexibility and closer center of mass (to the backbone) for alicyclic substituents.

Introduction

Chinai and co-workers[1-6] began a systematic study to document the effect of n-alkyl substituents on the chain flexibility of various poly(n-alkyl methacrylates) in the mid-1950s. More recently, Xu et al.[7] reported characteristic ratios (C_∞) for selected poly(n-alkyl methacrylates) up to docosyl. For cases where polymer tacticity is kept roughly constant, the trend is clear; increasing side-chain length leads to an increase in C_∞.

In this work, we report characteristic ratios and dilute solution properties for four series of poly(alicyclic methacrylates) with side groups covering the range from cyclobutyl to cyclododecyl. Since rotational isomeric state (RIS) models[8,9] have not yet been formulated for these polymers, results are compared with those for the poly(n-alkyl methacrylates) and are interpreted in terms of substituent size, flexibility, and distance of the center of mass from the polymer backbone.

Experimental Section

The monomers were synthesized by direct esterification of methacrylic acid with the appropriate alcohol in the presence of p-toluenesulfonic acid as a catalyst and methylene blue as inhibitor. All monomers were purified by distillation under reduced pressure with N,N'-di-β-naphthyl-p-phenylenediamine added to inhibit polymerization. Solution polymerizations were conducted under high-vacuum conditions in benzene at 50 °C with AIBN as initiator. The concentration of monomer was 10% (w/w), except in a few cases where 20% (w/w) solutions were employed, and the initiator concentration was varied between 0.001 to 1% (w/w). Five to six polymerizations were carried out for each monomer except cyclobutyl methacrylate, where two polymerizations were conducted. Polymer fractionation was carried out with toluene solutions with methanol as the nonsolvent.[10]

Tacticities were evaluated in C_6D_6 via 90-MHz ^{13}C NMR. Triad concentrations were determined by the intensities of both the carbonyl and methyl carbons.[11] Close agreement was obtained between the two methods, and average values are reported in Table I.

Table I
Tacticity of Polymethacrylates

polymer	*rr*	*mr* + *rm*	*mm*
PCBM[a]	65	32	3
PCPM[b]	66	32	2
PCOM[c]	63	34	3
PCDM[d]	63	34	3

[a] Poly(cyclobutyl methacrylate). [b] Poly(cyclopentyl methacrylate). [c] Poly(cyclooctyl methacrylate). [d] Poly(cyclododecyl methacrylate).

Polymer molecular weight characterization was done by using a combination of light scattering, membrane osmometry, and size-exclusion chromatography (SEC). Highly purified solvents were used in all dilute solution work. Refractive index increments were determined at 24 °C by using the Chromatix KMX-16 differential refractometer at a wavelength of 6328 Å. Values of 0.0975 and 0.0995 mL g^{-1} were found in tetrahydrofuran (THF) for poly(cyclobutyl methacrylate) (PCBM) and poly(cyclopentyl methacrylate) (PCPM), respectively. For poly(cyclooctyl methacrylate) (PCOM) and poly(cyclododecyl methacrylate) (PCDM) measurements in cyclohexane yield dn/dc values of 0.0977 and 0.0935 mL g^{-1}, respectively. Light scattering measurements were carried out under the same conditions with the Chromatix KMX-6 low-angle laser light scattering (LALLS) photometer. A Mechrolab Model 502 unit and a Knauer unit were used for the osmometry experiments; RC-51 membranes (from Wescan) were employed in toluene at 25 °C. Square root plots[12] were used for obtaining molecular weights from both LALLS and osmometry data. SEC measurements were carried out with a Waters 150C unit having a seven-column μ-Styragel set in stabilized THF at 1 mL min^{-1}.

Phase equilibria studies yielded Θ temperatures (T_Θ) via Shultz–Flory plots.[13] A typical plot is given in Figure 1 for PCDM in n-hexyl acetate (T_Θ = 35 °C). For PCBM and PCOM, respectively, Θ conditions were established in 1-butanol at 37.5 °C and 2-butanol at 45 °C. For PCPM the Θ temperature was derived from light scattering (Sofica) measurements of A_2 as a function of temperature in cyclohexane (T_Θ = 36 °C).

Intrinsic viscosities were measured in good solvents and under Θ conditions by using Cannon-Ubbelohde dilution viscometers with negligible kinetic energy corrections. Solutions with relative viscosities between 1.1 and 1.7 were used. Dilute solution characteristics of the samples are given in Tables II-V.

Results and Discussion

The second virial coefficient and weight-average molecular weight data of Tables II–V lead to the relationships described in Table VI. The exponents of −0.217 to −0.271 are consistent with the usual findings for flexible polymers in good solvents and with the suggestion of Berry and Casassa[14] that the limiting value of this exponent is ca. −0.25. Our values are somewhat larger, however, than the recent theoretical value of −0.2.[36]

From the intrinsic viscosity and weight-average molecular weight data (Tables II–V), we obtain the Mark–

Table II
Molecular Characteristics of Poly(cyclobutyl methacrylates)

sample	$10^{-4}\overline{M}_w$	$10^4 A_2$, mol cm^3 g^{-2}	$10^{-4}\overline{M}_n$	$[\eta]_{37.5°C}{}^{1\text{-butanol}}$, dL g^{-1}	k_H	$\overline{M}_w/\overline{M}_n{}^a$	$\overline{M}_w/\overline{M}_n{}^b$	$\overline{M}_z/\overline{M}_w{}^b$
F	31.15	3.88	22.6	0.255	0.73	1.3	1.2	1.3
G	15.2	4.35	13.3	0.18	0.84	1.1	1.1	1.1
A	13.9	4.32	12.1	0.17	0.74	1.1	1.3	1.3
J	9.25	5.40	8.57	0.14	0.74	1.1	1.1	1.1
B	7.49	5.38	6.80	0.13	0.82	1.1	1.2	1.2
K	4.83^c		4.13	0.10	0.62		1.2	1.1

[a] Absolute measurements. [b] SEC. [c] $\overline{M}_w = \overline{M}_n(\overline{M}_w/\overline{M}_n)_{SEC}$.

Table III
Molecular Characteristics of Poly(cyclopentyl methacrylates)

sample	$10^{-4}\overline{M}_w$	$10^4 A_2$, mol cm^3 g^{-2}	$10^{-4}\overline{M}_n$	$[\eta]_{36°C}{}^{\text{cyclohexane}}$, dL g^{-1}	k_H	$[\eta]_{30°C}{}^{\text{toluene}}$, dL g^{-1}	k_H	$[\eta]_{30°C}{}^{\text{dioxane}}$, dL g^{-1}	k_H	$[\eta]_{30°C}{}^{\text{MEK}}$, dL g^{-1}	k_H	$[\eta]_{30°C}{}^{\text{ethyl acetate}}$, dL g^{-1}	k_H	$\overline{M}_w/\overline{M}_n{}^a$	$\overline{M}_w/\overline{M}_n{}^b$	$\overline{M}_z/\overline{M}_w{}^b$
A	358	1.88		0.85	1.13	3.05	0.25	2.20	0.33	1.87	0.37	1.38	0.92		1.3	1.3
B	209	2.05		0.65	1.11	2.15	0.30	1.70	0.27	1.44	0.3	1.04	0.85		1.2	1.2
C	97.3	2.59		0.46	1.25	1.30	0.29	1.00	0.30	0.80	0.31	0.63	0.92		1.2	1.2
D	54.4	3.02	41.2	0.34	1.34	0.80	0.30	0.65	0.25	0.56	0.31	0.45	0.70	1.3	1.3	1.2
E	23.6	3.21	16.1	0.23	0.99	0.45	0.34	0.37	0.31	0.31	0.50	0.26	0.92	1.5	1.5	1.4
F	11.0	4.08	10.4	0.15	0.93	0.265	0.35	0.215	0.60	0.20	0.37	0.17	1.04	1.1	1.2	1.2
G	7.89	4.65	6.20	0.14	0.93	0.215	0.33			0.17	0.39	0.145	0.93	1.3	1.3	1.3
H	4.58	4.94	3.63	0.10	1.03	0.15	0.35	0.13	0.75	0.12	0.38	0.11	0.89	1.3	1.4	1.3
I	2.90	5.08	2.65			0.11	0.35	0.10	0.42	0.095	0.31	0.083	1.09	1.1	1.2	1.2

[a] Absolute measurements. [b] SEC.

Table IV
Molecular Characteristics of Poly(cyclooctyl methacrylates)

sample	$10^{-4}\overline{M}_w$	$10^4 A_2$, mol cm^3 g^{-2}	$10^{-4}\overline{M}_n$	$[\eta]_{45°C}{}^{2\text{-butanol}}$, dL g^{-1}	k_H	$[\eta]_{30°C}{}^{\text{toluene}}$, dL g^{-1}	k_H	$[\eta]_{30°C}{}^{\text{dioxane}}$, dL g^{-1}	k_H	$\overline{M}_w/\overline{M}_n{}^a$	$\overline{M}_w/\overline{M}_n{}^b$	$\overline{M}_z/\overline{M}_w{}^b$
A	418	0.89		0.74	0.55	2.70	0.54	1.21	0.71		1.6	1.4
B	137	1.20		0.43	0.63	1.29	0.45	0.591	1.00		1.7	1.6
C	119	1.30		0.40	0.69	1.13	0.32	0.547	0.50		1.7	1.6
D	42.7	1.63	34.8	0.24	0.94	0.54	0.44	0.310	0.53	1.2	1.4	1.6
E	21.4	1.89	18.4	0.17	0.80	0.35	0.53	0.220	0.42	1.2	1.3	1.3
F	12.1	2.47	9.11	0.13	0.91	0.24	0.41	0.156	0.83	1.3	1.4	1.3
G	6.63	2.70	6.19	0.099	1.84	0.16	0.55	0.124	0.72	1.1	1.2	1.2
F	3.05	3.41	3.00			0.099	0.25	0.080		1.0	1.3	1.2

[a] Absolute measurements. [b] SEC.

Table V
Molecular Characteristics of Poly(cyclododecyl methacrylates)

sample	$10^{-4}\overline{M}_w$	$10^4 A_2$, mol cm^3 g^{-2}	$10^{-4}\overline{M}_n$	$[\eta]_{35°C}{}^{n\text{-hexyl acetate}}$, dL g^{-1}	k_H	$[\eta]_{30°C}{}^{\text{toluene}}$, dL g^{-1}	k_H	$[\eta]_{30°C}{}^{\text{cyclohexane}}$, dL g^{-1}	k_H	$\overline{M}_w/\overline{M}_n{}^a$	$\overline{M}_w/\overline{M}_n{}^b$	$\overline{M}_z/\overline{M}_w{}^b$
A	475	0.74		0.71	0.56	2.35	0.63	2.00	0.61		1.5	1.4
B	120	0.94		0.355	0.45	0.89	0.30	0.80	0.79		2.1	1.9
C	65.7	1.18	47.7	0.260	0.53	0.60	0.30	0.53	0.44	1.4	1.5	1.5
D	35.4	1.27	29.9	0.195	0.47	0.38	0.35	0.34	0.54	1.2	1.4	1.3
E	11.9	1.80	8.03	0.115	0.81	0.185	0.47	0.18	0.49	1.5	1.7	1.4
F	9.84	1.77	7.27			0.165		0.156	0.74	1.4	1.4	1.5
G	5.12	2.05		0.075	2.0	0.103		0.105	0.70		1.5	1.3

[a] Absolute measurements. [b] SEC.

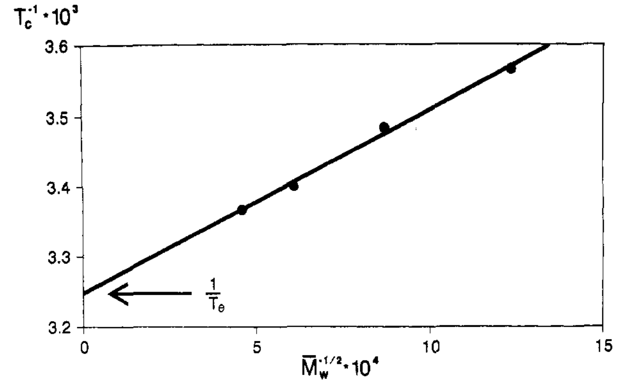

Figure 1. Determination of the Θ temperature for poly(cyclododecyl methacrylate) in *n*-hexyl acetate. The reciprocal of the critical temperature (T_c^{-1}) is plotted versus $\bar{M}_w^{-1/2}$ to obtain $1/T_\Theta$ as the intercept.

Table VI
Second Virial Coefficient–Molecular Weight Relationships ($A_2 = C\bar{M}_w^{\nu}$) for Polymethacrylates at 24 °C

polymer	solvent	10^3C	ν
PCBM	THF	9.12	−0.252
PCPM	THF	5.01	−0.217
PCOM	cyclohexane	5.56	−0.271
PCDM	cyclohexane	2.62	−0.234

Houwink–Sakurada (M-H-S) constants given in Table VII. The exponents obtained under measured Θ conditions are very close to 0.50, the value for unperturbed chains. Nevertheless, we chose to apply the Burchard–Stockmayer–Fixman[15–17] (B-S-F) extrapolation procedure to correct these data for small apparent departures from the Θ temperature. The unperturbed parameters thus derived are presented in Table VIII in terms of K_Θ where

$$K_\Theta = \Phi(\langle r^2\rangle_0/\bar{M}_w)^{3/2} \qquad (1)$$

$\langle r^2\rangle_0$ is the unperturbed mean-square end-to-end distance, and Φ is a universal hydrodynamic constant[18] for flexible unperturbed linear chains equal to 2.5×10^{21} [19–25] in cgs units.

From K_Θ, Flory's[8,9] characteristic ratio can be calculated from the relation

$$C_\infty = \lim_{n\to\infty} \langle r^2\rangle_0/nl^2 \qquad (2)$$

where n is the number of main-chain bonds of length l. C_∞ values are also given in Table VIII. Larger C_∞ values reflect increased hindrances to rotation about main-chain bonds, i.e., increasing departure from "freely jointed" character. The C_∞ results clearly show that an increase in the size of the alicyclic side group results in diminished chain flexibility for this family of polymers.

The rotational isomeric state model[8,9] has proven very useful for calculating configuration-dependent properties (such as C_∞) of macromolecules, including poly(methyl methacrylate).[26–29] Unfortunately, RIS models have not yet been developed for polymethacrylates with structurally complex side groups such as the polymers of this work.[30] Interpretation of our results in terms of existing RIS models is therefore not possible. It appears that the observed trend is caused by the increasing side group size on going from PCBM to PCDM. In other words, the increased hindrances to rotation on increasing ring size are sterically induced. It is important to mention here that tacticity of these polymers (Table I) is virtually unaffected by the choice of side groups.

It is also of interest to compare our results for alicyclic substituted polymethacrylates with results for their *n*-alkyl-substituted counterparts (Table VIII). In both series an increase in the number of carbons in the side group leads to an increase in C_∞. In addition, the data of Table VIII demonstrate that polymethacrylates with alicyclic side groups are less flexible than their *n*-alkyl counterparts with the same number of carbons in the side group. This effect can be ascribed to the diminished flexibility and closer center of mass (to the backbone) for alicyclic substituents.[34]

Table VII
Mark–Houwink–Sakurada Relationships for Polymethacrylates[a]

polymer	solvent	temp, °C	10^4K, dL g$^{-3/2}$ mol$^{1/2}$	α
PCBM	1-butanol	37.5	4.92	0.494
PCPM	cyclohexane	36	5.48	0.487
PCPM	ethyl acetate	30	1.94	0.588
PCPM	MEK	30	1.36	0.631
PCPM	1,4-dioxane	30	1.09	0.659
PCPM	toluene	30	0.838	0.696
PCOM	2-butanol	45	4.32	0.488
PCOM	1,4-dioxane	30	2.60	0.549
PCOM	toluene	30	0.870	0.677
PCDM	*n*-hexyl acetate	35	3.54	0.494
PCDM	cyclohexane	30	0.884	0.651
PCDM	toluene	30	0.603	0.687

[a] Values of K and α were determined by least-squares analysis. Correlation coefficients were always greater than 0.998.

Table VIII
Unperturbed Parameters for Polymethacrylates

polymer	10^4K_Θ,[a] dL g$^{-3/2}$ mol$^{1/2}$	C_∞[b]	C_∞(*n*-alkyl)[c]
PCBM	4.77	10.0	7.9–8.5
PCPM	4.78	11.2	
PCHM[d]	4.59	11.6	10.1–10.5
PCOM	3.77	12.1	9.6–10.4
PCDM	3.30	14.2	12.9–13.4

[a] Obtained from the Θ conditions data via the use of the B-S-F procedure. [b] The values of K_Θ were corrected for polydispersity[31] prior to the calculation of C_∞. These corrections were quite small (ca. 1.03). [c] Reference 32. [d] Poly(cyclohexyl methacrylate), ref 33.

The Huggins coefficients of Tables II–V deserve brief comment. Larger values of k_H are observed with decreasing solvent "quality", in accord with theory.[35] Values of k_H are also, at least to a first approximation, independent of molecular weight in all solvents investigated.

In summary, the flexibility of polymethacrylates with alicyclic side groups decreases with increasing size of the side group. In addition, for a constant number of carbons in the side group, higher characteristic ratios are found for alicyclic versus *n*-alkyl substituents. These effects are explained in terms of diminished flexibility and closer center of mass (to the backbone) for alicyclic substituents.

Registry No. PCBM, 118420-90-9; PCPM, 28298-90-0; PCOM, 28298-92-2; PCDM, 64328-84-3.

References and Notes

(1) Chinai, S. N.; Samuels, R. J. *J. Polym. Sci.* **1956**, *19*, 463.
(2) Chinai, S. N.; Guzzi, R. A. *J. Polym. Sci.* **1956**, *21*, 417.
(3) Chinai, S. N.; Bondurant, C. W. *J. Polym. Sci.* **1956**, *22*, 555.
(4) Chinai, S. N. *J. Polym. Sci.* **1957**, *25*, 413.
(5) Chinai, S. N.; Resnick, A. L.; Lee, H. T. *J. Polym. Sci.* **1958**, *33*, 471.
(6) Chinai, S. N.; Guzzi, R. A. *J. Polym. Sci.* **1959**, *41*, 475.
(7) Xu, Z.; Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1984**, *17*, 2303.
(8) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience; New York, 1969.
(9) Flory, P. J. *Macromolecules* **1974**, *7*, 381.

(10) Hadjichristidis, N. *Makromol. Chem.* **1977**, *178*, 1463.
(11) Mays, J. W.; Ferry, W.; Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1985**, *18*, 2330.
(12) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971; Chapter 7.
(13) Shultz, A. R.; Flory, P. J. *J. Am. Chem. Soc.* **1952**, *74*, 4760.
(14) Berry, G.; Casassa, E. F. *J. Polym. Sci., Part D* **1970**, *4*, 1.
(15) Burchard, W. *Makromol. Chem.* **1961**, *50*, 20.
(16) Stockmayer, W. H.; Fixman, M. *J. Polym. Sci.* **1963**, *1*, 137.
(17) Stockmayer, W. H. *Br. Polym. J.* **1977**, *9*, 89.
(18) Flory, P. J. *J. Chem. Phys.* **1949**, *10*, 51.
(19) McIntyre, D.; Wims, A.; Williams, L. C.; Mandelkern, L. *J. Phys. Chem.* **1966**, *66*, 1932.
(20) Berry, G. C. *J. Chem. Phys.* **1967**, *46*, 4886.
(21) Fukuda, M.; Fukutomi, M.; Kato, Y.; Hashimoto, T. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 105.
(22) Norisuye, T.; Kawahara, K.; Teramoto, A.; Fujita, H. *J. Chem. Phys.* **1968**, *49*, 4330.
(23) Yamamoto, A.; Fujii, M.; Tanaka, G.; Yamakawa, H. *Polym. J. (Tokyo)* **1971**, *2*, 799.
(24) Miyake, Y.; Einaga, Y.; Fukita, M.; Fukada, M. *Macromolecules* **1980**, *13*, 588.
(25) Hadjichristidis, N.; Xu, Z.; Fetters, L. J.; Roovers, J. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 743.
(26) Sundararajan, P. R.; Flory, P. J. *J. Am. Chem. Soc.* **1974**, *96*, 5025.
(27) Sundararajan, P. R. *J. Polym. Sci., Polym. Lett. Ed.* **1977**, *15*, 699.
(28) Vacatello, M.; Flory, P. J. *Macromolecules* **1986**, *19*, 405.
(29) Sundararajan, P. R. *Macromolecules* **1986**, *19*, 415.
(30) Development of RIS models for polymers with complex side groups has been hindered because of the complifications inherent in taking into account the effects of various substituent conformations on polymer chain statistics.
(31) Bareiss, R. E. *Polymer Handbook*, 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; Interscience: New York, 1975; pp iv–115.
(32) Brandrup, J., Immergut, E. H., Eds. *Polymer Handbook*, 2nd ed.; Interscience: New York, 1975; Part IV.
(33) Hadjichristidis, N.; Touloupis, C.; Fetters, L. J. *Macromolecules* **1981**, *14*, 128.
(34) Mays, J. W.; Hadjichristidis, N. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1988**, *C28(3&4)*, 371.
(35) Bohdanecky, M.; Kovar, J. *Viscosity of Polymer Solutions*; Elsevier: Amsterdam, 1982.
(36) De Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University: Ithaca, NY, 1979.

Synthesis and Characterization of Liquid Crystalline Polymethacrylates, Polyacrylates, and Polysiloxanes Containing 4-Hydroxy-4′-methoxy-α-methylstilbene Based Mesogenic Groups

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ABSTRACT: The synthesis and characterization of polymethacrylates and polyacrylates containing 4-hydroxy-4′-methoxy-α-methylstilbene side groups attached through flexible spacers containing 11, 8, 6, 3, and 2 methylenic units and of the polysiloxanes containing the same mesogenic group connected through flexible spacers containing 11, 8, 6, and 3 methylenic units, respectively, are described. All polymers exhibit thermotropic liquid crystallinity. The nature of the mesophase is determined by the spacer length. However, the nature of the polymer backbone determines the thermal stability of the mesophase and the ease of the side-chain crystallization. That is, for the same spacer length and similar polymer molecular weight, the most flexible polymer backbone leads to the highest isotropization temperature and the highest ease of side-chain crystallization. This last effect may lead to transformation of enantiotropic mesophases into monotropic mesophases.

Introduction

Previous publications from our laboratory have suggested that side-chain liquid crystalline "copolymers" of monomer pairs containing constitutional isomeric mesogenic units are useful both to depress side-chain crystallization of polymers containing long flexible spacers and to obtain qualitative information about the degree of decoupling.[1–4] This idea was based on the fact that mesomorphic phases of the same type are usually miscible, while crystallization of two isomers is a more difficult process. Consequently, for a single-phase side-chain liquid crystalline copolymer based on constitutional isomeric side groups, we would expect side-chain crystallization to be depressed. Alternatively, for a microphase-separated side-chain liquid crystal polymer,[5–7] we would expect to observe independent crystallization of each isomer in part.[3]

Therefore, copolymers of constitutional isomeric groups may represent a chemical sensor which provides at least qualitative information on the dynamics of side-chain liquid crystalline polymers. If this assumption is correct, these copolymers can offer a qualitative and complimentary approach to the study of the dynamics of side-chain liquid crystalline polymers.[8–13]

The experiments performed so far were done with side groups based on 4-methoxy-4′-hydroxy-α-methylstilbene and 4-hydroxy-4′-methoxy-α-methylstilbene constitutional isomers. However, all monomer mixtures were prepared directly as mixtures of constitutional isomers, since they were synthesized by the monomethylation of 4,4′-dihydroxy-α-methylstilbene.[1–3] Although the molar ratio between the two constitutional isomeric side groups was determined by spectropical methods, no information about the behavior of each of the two homopolymers based on each individual constitutional isomer was available. In order to obtain a quantitative interpretation of these copolymers' behavior, the synthesis and characterization of the homopolymers based on each of the two constitutional isomers are mandatory. The synthesis and characterization of the polymethacrylates, polyacrylates, and polysiloxanes containing mesogenic groups based on 4-methoxy-4′-hydroxy-α-methylstilbene and flexible spacers containing 11, 8, 6, 3, and 2 methylenic units and of the corresponding polysiloxanes containing 11, 8, 6, and 3 methylenic units as flexible spacers were reported in a previous paper.[4]

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