the glycolate carboxyl and malate hydroxy groups of the monomer. Random transesterification[10] to give the random sequence or to propagate the branch seemed to be negligible under the present polymerization conditions.[16] Since the polymerization temperature and time were relatively low, as compared to those of the polymerization of glycolide and lactide, the rate of the transesterification involving the polymer chain and pendant esters might be much slower than that of the ring opening of **10**. The molecular weight distributions of the polymers were relatively broad, which may be attributed to the reversible depolymerization process that has been known in this type of ring-opening polymerization.[5b,10]

The polymer **11** was subjected to catalytic hydrogenolysis by using platinum oxide and palladium carbon as the catalysts.[6,7] For example, 0.09 g of **11** (sample, the product of run 8) was dissolved in a mixed solvent (20 mL) of methanol/ethyl acetate (1:3) and was reacted with hydrogen at atmospheric pressure and at 30 °C in the presence of 10 mg of PtO_2 for 4 h. After the theoretical quantity of hydrogen was absorbed, the catalyst was filtered off and the filtrate was poured into an excess of diethyl ether to isolate the white crystalline product of **12** in quantitative yield: mp 85–110 °C, $[\alpha]^{25}{}_D = -43.5°$ (in acetone, $c = 0.2$ g/dL); M_n (by GPC) 1200 (calcd M_n = 1320). The characterization of its structure is shown in Table II. The benzyl groups of **11** were completely deprotected and the formation of the alternating copolymer **12** consisting of glycolic and (*S*)-malic acids was confirmed. Since the polymer was water soluble and self-hydrolizable,[15] it should have some potential applications as a new bioresorbable material. We are now studying the polymerization mechanism of **10** in more detail as well as the copolymerization of **10** and other lactones.

Registry No. **7**, 56-84-8; **8**, 66178-06-1; **9**, 117098-33-6; **10**, 117098-34-7; **10** (homopolymer), 117098-35-8; $PhCH_2OH$, 100-51-6; $BrCH_2COCl$, 22118-09-8.

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(14) If the polymer had a random sequence, the signals of the main-chain carbonyls should be split into four lines corresponding to the four possible triads (e.g., G–*M*–G, G–*M*–M, M–*M*–G, and M–*M*–M), as observed in the copolymer of glycolide and lactide.[10b]

(15) The polymer **12**, obtained by the catalytic hydrogenolysis of **11**, was dissolved in a mixture of acetone/water (1:1 in volume) and hydrolyzed to the constituents hydroxy acids at 50 °C. After 3 days, the hydrolysis was complete. Then the solution was directly subjected to the measurement of the optical rotation of (*S*)-malic acid contained. The value $[\alpha]^{25}{}_D$ observed was −3.2° (c = 0.12 g/dL). The optical rotation of the authentic solution containing the same concentrations of (*S*)-malic acid (c = 0.12 g/dL) and glycolic acid (c = 0.07 g/dL) in the same mixed solvent was found to be −3.3°. Since both values were identical within experimental error, it was supposed that no racemization of the asymmetric center had occurred during the reactions.

(16) When the bulk polymerization was carried out at higher temperature, e.g., 180 °C, for prolonged time, randomization of the sequence was found. The polymer obtained in this case showed complex signals for the methylene protons of the G units in its ^1H NMR spectrum.

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Verification of the Contour Length Fluctuation Mechanism in Polystyrene/Polyisoprene Block Copolymers by an NMR Experiment

In a series of previous papers[1-3] we have developed the three-component/three-block concept of chain fluctuations. It takes into account the special structure/dynamics relationship caused by topological restraints such as the tube.[4] The outstanding elements of this dynamic scheme are the reptation[5] and the contour length fluctuation[6] mechanisms.

The concept has been tested by studies of diverse dependences of NMR quantities. Thus we were able to describe the frequency,[7] molecular weight,[3] temperature,[8] and concentration[9] dependences of NMR relaxation times in melts or solutions of homopolymer standards. Special limiting cases characteristic for motions restricted by the tube topology could well be identified. The existence of characteristic molecular weights, for instance, has been explained in this way. The so-called critical molecular weight, which is well-known in rheology,[10] in particular can be understood as a crossover from Rouse-like to reptational dynamics mediated by the influence of contour length fluctuation.[1] In structural terms, one can speak of three dynamic chain blocks, the lengths of which vary nonlinearly with molecular weight.[1,2,6] Thus at low molecular weights, the end blocks with Rouse-like dynamics are expected to dominate, while in the limit of long chains the reptational dynamics of the central block becomes relevant.

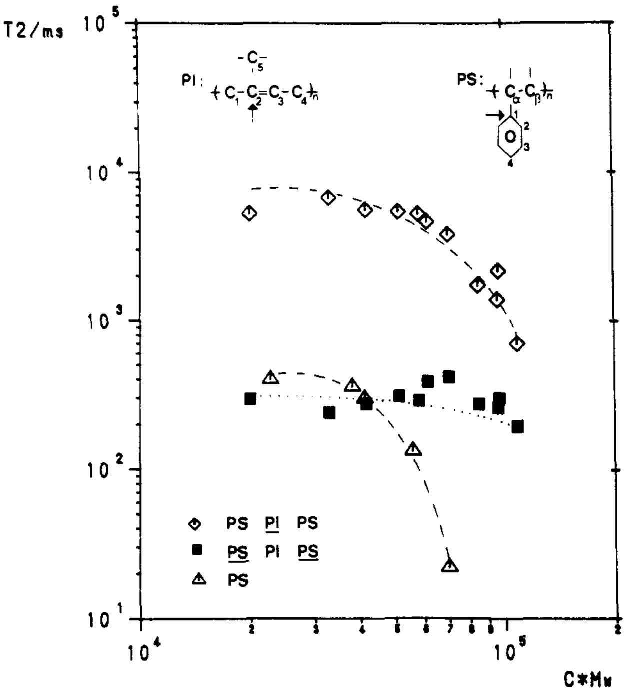

Figure 1. Dilution behavior of the transverse relaxation time at 80 °C of the quarternary carbons of a PS–PI–PS block copolymer and a PS homopolymer dissolved in toluene. The data are plotted versus CM_w, where C is the volume fraction of the polymers. The weight averages of the molecular weight, M_w, were 110 000 and 100 000 for the co- and the homopolymer, respectively. The two sets of T_2 data of the copolymer refer to the quarternary carbons of the blocks underlined in the plot.

The same type of crossover is expected to occur in dilution experiments from melts to dilute solutions.[1,9]

Previously we have shown that the transverse relaxation time T_2 is particularly suited for the detection of such a dilution crossover.[9] The aim of the present study is to differentiate the behavior of the chain-end blocks (expected to obey Rouse-like dynamics in the melt) from the central chain blocks (subject to topological tube restraints in the melt). If the contour length fluctuation hypothesis that the chain-end blocks obey Rouse-like dynamics in the melt irrespective of the total chain length is true, then no dilution crossover should appear for these blocks, in contrast to the central block.

As a suitable test polymer, permitting the distinction of the corresponding blocks, we have used a polystyrene (PS)/polyisoprene (PI) copolymer of the sequence PS–PI–PS. The chain-end blocks have in effect been labeled by polystyrene blocks. The NMR distinction itself is due to ^{13}C lines characteristic of the two polymer constituents. For comparison, a second dilution experiment has been carried out with polystyrene as a homopolymer.

The copolymer has been prepared by Polymer Standard Service, Mainz, using the anionic polymerization method. The weight-average molecular weight of the total polymer is $M_w = 110000$ with a ratio $M_w/M_n = 1.09$. The molecular weight of the polystyrene blocks is $M_w = 1000$ for each chain-end block. The numbers of monomers thus are related as 10:1600:10 for the PS–PI–PS sequence. The length of the end blocks is much less than the root-mean-square fluctuation of the contour length. Thus the full effect of contour length fluctuation should reveal itself in the behavior of these blocks.

The resonances of the quarternary carbons of the two-block species are of special interest because their transverse relaxation times are sensitive to very slow motions.[11] The reason is that the "local fields" acting on them due to couplings are low. The polyisoprene block consists of about 96% cis- and trans-1,4-bond structures. About 4% are 3,4- instead of 1,4-compounds.

The resonance of the quarternary carbon of the polystyrene parts appears at 146 ppm relative to TMS. The polyisoprene block leads to two resolved lines of quarternary carbons at 134.7 and 146.9 ppm for the 1,4- and 3,4-monomers, respectively. Thus the 3,4-monomer line overlaps the polystyrene resonance. A distinction is nevertheless possible, because the transverse relaxation times deviate considerably. The relaxation curve of the superimposed 146 ppm lines could easily be decomposed into two exponentials. The T_2 values of the rapidly decaying component ranged from 190 to 420 ms. The slowly decaying component led to relaxation times practically equal to those measured with the cis-1,4 isoprene quarternary carbon line. The shorter T_2 component hence must be attributed to polystyrene. We are thus able to measure T_2 specifically for the two types of blocks.

The samples were evacuated overnight and then dissolved in toluene, yielding clear solutions. The measurements were carried out after a 10-day annealing period. Figure 1 shows the T_2 data measured at 80 °C.

The polyisoprene block data indicate the crossover from the molten state to dilute solutions by a strong increase of the T_2 values from about 600 ms to 6 s. This corresponds to the reduction and final loss of the tube restraints connected with dilution. Similar behavior has been found with the polystyrene homopolymer. Here the relaxation times are reduced by 1 order of magnitude due to the stronger local interactions of the quarternary carbons.

The data for the polystyrene blocks of the copolymer show quite different behavior. Practically no concentration dependence has been found. This means that the polystyrene segments are subject to the same dynamics in the molten and in the dilute state as far as concerns the time scale of the quarternary carbon relaxation.

We conclude that the chain-end blocks do not sense the topological restraints of entangled systems. Thus a crucial consequence of the contour-length fluctuation model has been confirmed. This paper is the first report of a series of experiments with block copolymers, being carried out at present. The systematic variation of the block lengths and positions is expected to provide a quantitative measure of the "topological restraint profile" along a chain.

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