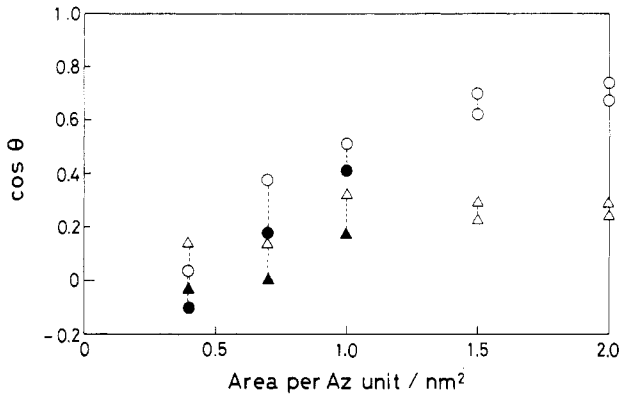

Figure 2. Contact angle of water as a function of two-dimensional Az density on substrates. The contact angle of a droplet was measured after 1 min after placing. The 6Az10-PVA monolayer was deposited onto unmodified (circles) and ethyl-silylated (triangles) glass surfaces. Of the paired points, the upper and the lower correspond to the data for *cis*- and *trans*-Az surfaces, respectively. Open and closed symbols indicate LC alignment of parallel and homeotropic monolayers, respectively.

cell upon alternate exposure to UV (365 nm) and visible (436 nm) lights at room temperature. These changes are evidently induced by the photoisomerization of the surface Az unit. *trans*-Az gave the homeotropic LC alignment and no polarized 633-nm light passed through the cell, and as the Az isomerized to the cis form on UV irradiation, parallel alignment was induced resulting in a bright LC cell. The reverse occurred upon visible light. This proves that only Az monolayer is sufficient to control the LC alignment. Distance between the polymer backbone and Az unit was an important factor for the response. Monolayered 6Az*n*-PVA with longer methylene spacers (n = 5, 10) gave photoresponsive LC cells, whereas, for the polymer with n = 1, no responding behavior was observed. LC cells constructed with buildup multilayers of 6Az10-PVA LB films (3–9 layers deposited in Y-mode) also indicated almost identical transmittance changes and response times, suggesting that the surface layer in contact with LC molecules induces the LC alignment change. The occupying area of Az unit (A_{oc}) of 6Az10-PVA on the substrate surface was changed from 0.4 to 2.0 nm^2 by controlling the monolayer area on the water subphase. In this experiment, clean (unmodified) and ethyl-silylated[8] glass surfaces were used to evaluate the influence of the surface energy. Figure 2 indicates the relationship between A_{oc} and wettability for water (θ: contact angle of a droplet) and the LC alignment under the given conditions. For both series of the glass surface, increasing the Az density reduced the hydrophilicity of the surface and, for identical samples, conversion of Az from the trans to the cis form enhanced the wettability. When A_{oc} was 0.4 nm^2, the two sets of glass surfaces gave almost the same wetting property, and as A_{oc} increased, more hydrophilic surfaces were obtained for the unmodified glasses than the ethyl-silylated ones. These results are suggestive of good covering of the amphiphilic polymer at the high Az density and greater exposure of the substrate surface at lower density. LC responses were observed when A_{oc} was less than 1 nm^2, irrespective of the magnitude of the wettability, implying that the occurrence of LC response is primarily determined by A_{oc} and that arguments with macroscopic thermodynamic parameters[2,9] are less significant in the present system.[10] Our results support the proposal of Hiltrop and Stegemeyer[11] on the orientation of LCs on solid substrates coated with amphiphilic monolayers that the alignment strongly depends on the parameters, such as molecular structures of both the amphiphilic molecules and the LC molecules and packing density of the amphiphilic monolayer.

Our current efforts are being focused on the dependence of the chemical structure of Az derivatives on the LC response behaviors since subtle differences in the interaction mode between the photochromic layer molecules and LC molecules may lead to significant changes in LC alignment behaviors.

Registry No. DON 103, 115288-48-7; 6Az10-PVA, 121886-84-8; 6Az5-PVA, 121886-83-7; 6Az1-PVA, 120112-81-4.

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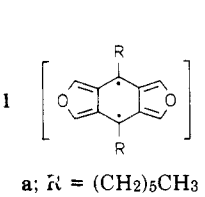
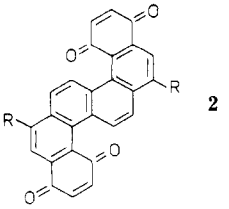
Ribbon-Shaped Structures via Repetitive Diels–Alder Reaction. A Polycatafusene

We are involved in the synthesis of ribbon (ladder) polymers, which can be considered as part of the graphite lattice.[1,2] Recently, we have proposed a route into this intriguing class of polymers that is based on repetitive Diels–Alder (DA) reactions of the bifunctional diene 1 and the bifunctional dienophile 2.[3] In the first step, this route



a; R = $(CH_2)_5CH_3$
b; R = $(CH_2)_{11}CH_3$



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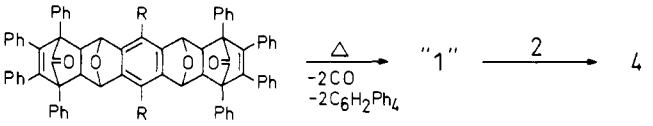
Scheme I



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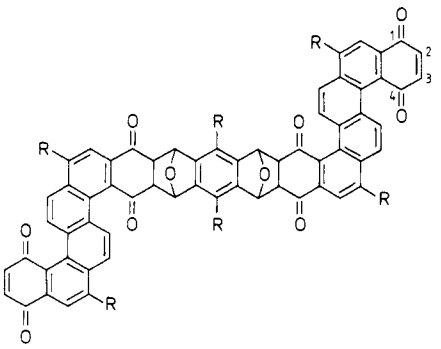
leads to ribbon polymers with regularly disrupted π-conjugation, so as to have materials that could certainly be handled under conventional laboratory conditions.[4] To keep the polymers soluble, and thus characterizable and processable, we attached alkyl chains to the monomers, a method that proved very effective in related cases.[5] Model studies provided good evidence for the feasibility of our strategy; the observed conversions were very high and all compounds prepared, including the 15-ring system, **3**, were soluble in common organic solvents at room temperature.[3] As an extension of this work, we now present the synthesis and the structure proof of ribbon polymer **4**, a poly[(0,0,0,1,1,2,2)catafusene(0,0)] derivative.[6-8]



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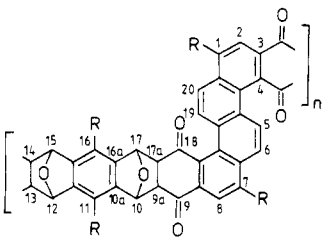

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Reaction of monomer **2a**, which is accessible in gram amounts,[2] with 1 equiv of **5a** gave a slightly yellow powder (yield 63%) to which we ascribe structure **4a** (Scheme I). Polymer **4a** turned out to be only sparingly soluble in chloroform; hence, its structure was proved by means of ^{13}C CPMAS-NMR spectroscopy (Figure 1).[9] Figure 1a shows the high-resolution ^{13}C NMR spectrum of the 15-ring model compound **3b**, comprising the various possible isomers (exo/endo, syn/anti, cisoid/transoid).[10] Regardless of this complex mixture of isomers, the spectrum of **3b** could be assigned unequivocally.[3] Its most interesting features are signals of the carbonyl end groups at δ = 185.5 and δ = 186.8. Comparison of this spectrum with the solid-state spectrum of polymer **4a** (Figure 1b) reveals striking similarities and establishes the proposed structure of **4a**. Note that the only significant difference in these two spectra is the lack of end-group signals of polymer **4a**.

Even though this result indicates that repetitive DA methodology in certain cases is a useful method for the preparation of ribbon topologies, it is unsatisfactory in relation to the desired solubility. Consequently, we utilized precursor **3b** and bisdienophile **2b**, both of which have

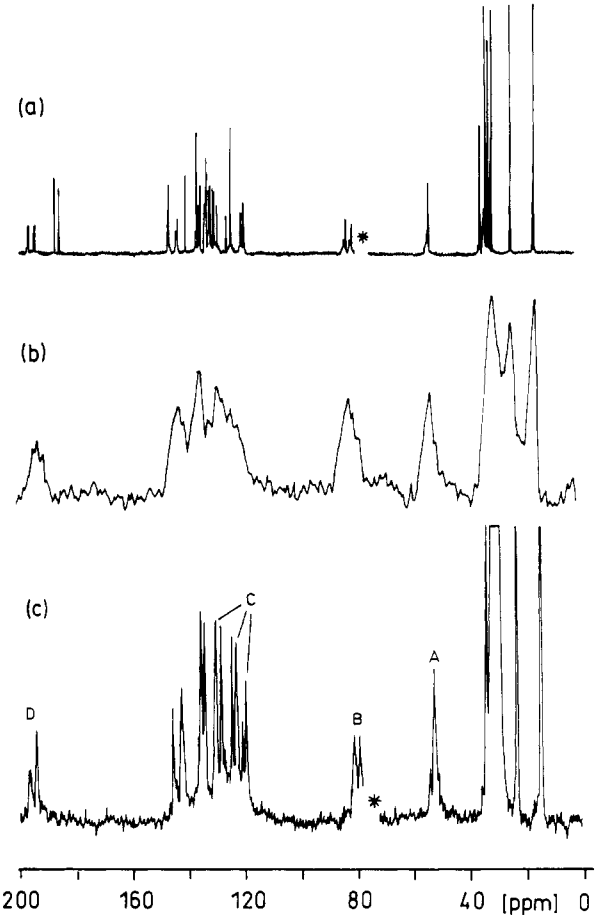

Figure 1. High-resolution ^{13}C NMR spectra ($CDCl_3$) of compound **3a** (a) and polymer **4b** (c) and the ^{13}C CPMAS-NMR spectrum (neat) of polymer **4a** (b). In spectra (a) and (c) the solvent signals are erased for clarity (*). The assignment of the signals in (c) is as follows: A, C-9a, -13, -14, -17a; B, C-10, -17, -12, -15; C, tertiary aromatic C's; D, C-9, -18 and the oxomethylene groups at C-3, -4.

dodecyl chains, and, in fact, the analogous procedure (Scheme I) gave a highly soluble material (yield 78%) whose high-resolution ^{13}C NMR spectrum is shown in Figure 1c. The similarity of spectrum (c) with spectra (a) and (b) again strongly suggests the structure of polymer **4**. The partial assignment of the signals of polymer **4b** was established on the basis of known shifts of various model compounds[3] and is in full agreement with the information obtained from a DEPT spectrum.

By the accuracy of spectrum (c), ribbon polymer **4b** still contains all epoxy bridges and no dehydration has taken place. On the one hand, these epoxy bridges help to increase the solubility of such rigid ribbons; on the other hand, they give rise to a vast number of isomers. Complete dehydration of polymer **4b**—the envisaged next step in this project—reduces the number of isomers to 2^n, where n is the number average degree of polymerization $\bar{P}_n$.[11] At present we are not able to give a reliable assessment for $\bar{P}_n$. It should, however, be mentioned that neither the ^1H nor the ^{13}C NMR spectrum of **4b** shows end-group signals, indicating a $\bar{P}_n > 10$. GPC curves (1,2-dichlorobenzene, 20 °C) obtained from the soluble part of polymer **4a** and those obtained from polymer **4b** indicate a monomodal distribution. The retention time of **4a** is significantly shorter than that of the coinjected 15-ring model compound **3a**. Since no appropriate GPC standard for rigid polymers is available, a quantitative treatment of the data could not be undertaken.[12] Viscosity measurements (toluene, 20 °C) with polymer **4b** gave $[\eta]$ = 0.11 dL/g. A

detailed investigation of this matter will be published in a full account.

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(8) A suspension of **5** (1.0 mmol; **a**, 1.15 g; **b**, 1.32 g) and **2** (1.0 mmol; **a**, 0.55 g; **b**, 0.73 g) in 10 mL of tetralin is heated under nitrogen to 180 °C until the evolution of carbon monoxide ceases (10 min). Then the solvent is removed in vacuo, the residue is dissolved in chloroform (**a**, 300 mL; **b**, 100 mL), and polymer **4** is precipitated from this solution with methanol. After a second dissolution/precipitation cycle pure **4** (**a**, 0.55 g (63%); **b**, 0.95 g (78%)) is obtained as slightly yellow powder. The analytical and spectroscopical data are given for polymer **4b** only. IR: ν 1680 (s), 1645 (m) cm^{-1}; UV (chloroform): λ_{max} (ϵ) = 320 (40 700), 390 (7900). ^{1}H NMR (300 MHz, CD_2Cl_2; all lines are very broad and unstructured): δ 0.4–2.3 (92 H), 2.4–3.9 (12 H), 5.7–6.5 (4 H), 7.6–8.5 (6 H). ^{13}C NMR (75 MHz, $CDCl_3$): see Figure 1. Elem anal. Calcd for $(C_{84}H_{114}O_6)_n$ (MW 1219.8): C, 82.71; H, 9.42; O, 7.87. Found: C, 81.26; H, 8.87; O, 7.59.
(9) TOSS pulse sequence; spinning frequency 2.955 kHz; neat; 20 °C; standard, TMS external.
(10) From the ^{13}C NMR spectrum of **3b**, it cannot be deduced whether all possible isomers are formed. The existence of a complex mixture of isomers certainly helps the objective to obtain soluble material.
(11) The incoming monomer **2** has two choices of orientation (cisoid/transoid) relative to the growing chain, if all isomers caused by the stereochemistry of the epoxy bridges are neglected.
(12) From a VPO measurement (toluene, room temperature) a lower limit for $\bar{P}_n$ is obtained: $\bar{M}_n$ = 8050 ($\bar{P}_n$ = 7).

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Dynamic Behavior in Ternary Homopolymer Solutions Using Dynamic Light Scattering

A recent communication[1] described dynamic light scattering (DLS) experiments on the homopolymeric polyisobutylene system PIB_1/PIB_2/chloroform, in which one polymer was present at semidilute concentration. The purpose was to explore the consequences of the recent thermodynamic theory of Benmouna et al.[2-4] for diffusion in ternary polymer solutions. Their result follows a line of development from the earlier studies of Phillies[5,6] and subsequently Pusey et al.[7] on dilute solutions of hard spheres of different sizes who had also demonstrated the possibility of simultaneously isolating the collective diffusion coefficient and the self-diffusion coefficient, although different arguments were used.

It was shown that if the respective diffusion coefficients differ sufficiently, two relaxation processes, arising from the modulation of the signal for the one polymer due to the presence of the second, should be observable. Benmouna et al. found that one obtains the collective diffusion coefficient (D_c) of the matrix (semidilute) polymer on the one hand and the interdiffusion coefficient (D_I) of the other and gave explicit expressions for these quantities as a function of concentration. It is important that by using a trace amount of the probe chain its self-diffusion coefficient may be measured. The following experiments reveal the potential of this approach, which forms a useful complement to existing techniques for determining polymer self-diffusion coefficients in semidilute solutions, viz., pulsed-field-gradient NMR (PFG NMR) and forced Rayleigh scattering (FRS).

We have used a broad-band autocorrelator (an ALV multibit, multi-τ, model employing 23 simultaneous sampling times and 191 exponentially spaced channels) together with a newly developed method for Laplace inversion to give the decay time spectrum covering wide spans in delay time, typically 6–8 decades. It was found possible to determine the self-diffusion coefficient for the trace component with good precision for a wide range of relative molecular weights of probe and matrix chains when using a concentration of the probe chain of less than 1% w/v since in this concentration range D_{probe} has a negligible dependence on its own concentration.[1] There will, of course, always be a (in fact, narrow) range of relative molecular weight where the components cannot be separated owing to the noise inherent in the data.

We have used a new constrained regularization calculation REPES[8] to obtain the decay time distributions. The algorithm differs from CONTIN[9] in that the program directly minimizes the sum of the squared differences between the experimental and calculated $g^{(2)}(t)$ function using nonlinear programming. We selected the a priori chosen parameter P ("probability to reject") = 0.5. In each solution the moments of the peaks are given in the output, yielding the relative amplitude and frequency of each resolved component. The distributions were observed to be closely similar to those obtained using CONTIN with a similar degree of smoothing and the maximum entropy method, MAXENT.[10,11]

Examples of the decay time distributions have been given in ref 1. Peak assignments were confirmed[1] using PFG NMR to independently determine the probe and matrix self-diffusion coefficients in the binary systems.

In the DLS experiments, two extreme cases were examined and are described below:

(1) the self-diffusion of large ($M = 4.9 \times 10^6$) probe chains in semidilute solutions of low MW polymers as a function of the concentration of the latter;

(2) the self-diffusion of small chains in semidilute solutions of the high MW matrix chains with the added criterion that the radius of gyration of the probe exceed the correlation length of the matrix polymer in the semidilute range.

In the experiments under (1), diffusion was approximately described by the Stokes–Einstein (S–E) equation; i.e., the product $D\eta$ was almost independent of the con-

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