Cooperative structure formation by combination of covalent and association chain polymers: 4. Designing functional groups for supramolecular structure formation

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(Received 17 July 1990; accepted 10 September 1990)

A small number of polar functional groups are attached to polybutadiene by a polymer analogous reaction. Depending on their molecular structure, different degrees of supramolecular ordering result from the aggregation of these polar groups. In the case of phenylurazole units, which carry a single site for hydrogen-bond complexation, binary contacts are formed; whereas linear association chain structures are formed in the case of polybutadiene carrying phenylurazole units additionally substituted with a carboxy group in *meta* or *para* positions of the phenyl ring. In the latter case, association chains aggregate cooperatively to an ordered supramolecular structure. The different structural features are evident in the stress–strain properties of these thermoplastic elastomers.

(Keywords: polybutadiene; thermoplastic elastomers; functional polymers; statistical copolymer)

INTRODUCTION

In previous papers of this series we have reported on supramolecular structure formation of polar groups in a polybutadiene matrix. The polar groups are attached to the chain by a polymer analogous reaction[1–4]. The basic structural elements are hydrogen bonds between the functional groups. Similar to biological systems the hydrogen-bond complexes are stabilized by the formation of extended junction zones based on the interacting sites.

The system where cooperative structure formation is observed is obtained by polymer analogous ene reaction of 4-(3,5-dioxo-1,2,4-triazolin-4-yl)benzoic acid (**2**) with polybutadiene (PB–U4A), where the abbreviation represents polybutadiene carrying phenylurazole units additionally substituted with a carboxy group in *meta* (U3A) or *para* (U4A) positions of the phenyl ring.

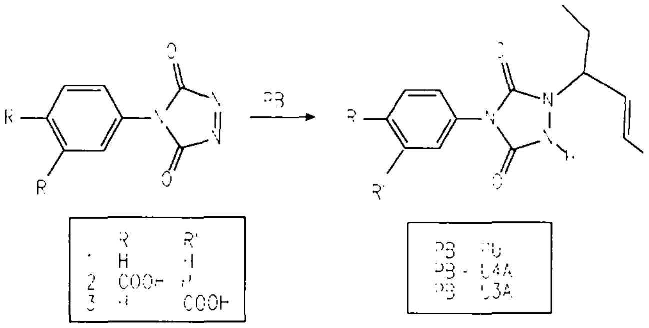
The functional groups are distributed statistically along the polymer backbone. The degree of modification, given in mol% with respect to moles of PB repeat units, is kept low—in all cases $\leqslant 10\%$.

In the resulting modified polymers (PB U3A, etc.) the heterocycle (urazole) and in PB-U3A and PB–U4A the additional carboxy group are able to form strong hydrogen-bond complexes.

The properties of polybutadiene modified with **2** are interesting from a material science as well as from a fundamental research oriented point of view. The principle realized here is ordering of statistically distributed moieties in the polymer melt. The difunctional groups form an association chain by hydrogen bonding. X-ray structure analysis[5] of a low-molecular-weight model compound proves that binary acid acid and urazole–urazole contacts are the dominating hydrogen-bond motifs acting in the polymer matrix.

PB samples modified with $\geqslant 0.5$ mol% of **2** show an endothermic transition at about 80°C (d.s.c.). This 'melting' is related to the breakdown of an ordered supramolecular structure. Beside d.s.c. further experimental evidence from SAXS, i.r. and d.m.a. has been gathered to get a more detailed picture of the structural organization.

From natural systems it is well known that, owing to the directed nature of hydrogen bonds, the molecular 'design' of the single moieties has a strong influence on the resulting structure and therefore on the specific functions of biomacromolecules. To check whether an analogy to biological systems is given in the present synthetic system, and to confirm that hydrogen bonds are the dominating parameter for structure formation, we synthesized and attached the *meta* isomer **3** to PB. The position of the carboxy substituent at the aromatic ring is changed from the *para* to the *meta* position



Scheme 1

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(relative to the heterocycle). Comparison of the resulting material properties will show whether or not it is possible to control properties by the architecture of the functional groups. This paper is the first approach to understand the structural features that govern structure formation in these statistical copolymers.

EXPERIMENTAL

Melting points are uncorrected. ^1H n.m.r. spectra were measured using a Bruker WP 80 CW spectrometer. Elemental analysis was carried out in the Microanalytical Laboratory of the Institut für Makromolekulare Chemie (Freiburg).

Synthesis of 3-(ethoxycarbonylsemicarbazoyl)benzoic acid ethyl ester

To a solution of 5 g (30.27 mmol) ethyl 3-aminobenzoate (Aldrich) dissolved in 300 ml CH_2Cl_2, a solution of 3 g (10.1 mmol) of bis(trichloromethyl)carbonate (triphosgene) is added under stirring at room temperature. The formed precipitate dissolves upon heating. After 3 h heating to reflux, the solvent is removed and the raw product is dissolved in 100 ml of dry toluene. This solution is added to a solution of 3.15 g (30.27 mmol) ethyl carbazate in 150 ml toluene under vigorous stirring and the resulting mixture is then heated to reflux for 2 h. After cooling, the precipitated product is filtered and dried under vacuum.

Yield: 7.87 g (88%).

M.p.: 139 C.

Elemental analysis (calculated values in brackets): C, 52.86 (52.87); H, 5.70 (5.80); N, 14.00 (14.23).

^1H n.m.r.: 1.27 ppm (6H, t, $2CH_3$); 4.1 ppm (2H, q, CH_2); 4.3 ppm (2H, q, CH_2); 7.6 ppm (3H, m, aromat.); 8.1 ppm (1H, s, aromat.); 8.2 ppm (1H, s, NH); 8.9 ppm (1H, s, aromat.); 9.05 ppm (1H, s, NH).

I.r. (KBr): 3360 (m), 3240 (m), 2970 (w), 2920 (w), 1720 (vs), 1685 (vs), 1640 (m), 1600 (s), 1590 (s), 1555 (vs), 1480 (m), 1430 (w), 1360 (m), 1340 (m), 1320 (m), 1300 (s), 1275 (s), 1230 (vs), 1160 (w), 1100 (m), 1070 (m), 1055 (m), 1015 (w), 990 (w), 930 (w), 890 (w), 870 (w), 860 (w), 840 (w), 750 (s), 680 (m) [cm^{-1}].

Synthesis of 3-(3,5-dioxo-1,2,4-triazolidin-4-yl)benzoic acid

First 0.93 g (3.15 mmol) of 3-(ethoxycarbonylsemicarbazoyl)benzoic acid ethyl ester are dissolved in 100 ml tetrahydrofuran (THF) (P.A.). After addition of 560 mg (10 mmol) KOH dissolved in 100 ml of a 1:1 THF/water mixture, the solution turns yellow. Under stirring this mixture is heated to reflux for 2 h. After cooling to room temperature semi-dilute HCl is added until pH 1 is reached. Upon removal of THF the product precipitates and is filtered and washed with cold water prior to drying under vacuum.

Yield: 0.5 g (71%).

M.p.: 290 C (decomposition).

Elemental analysis: C, 48.57 (48.88); H, 3.17 (3.19); N, 18.82 (18.99).

^1H n.m.r.: 7.5 8.1 ppm (4H, m, aromat.); 11.2 ppm (3H, br, s, COOH, NH).

I.r. (KBr): 3600 2500 (OH), 3320 (m), 3250 (vs), 3080 (w), 2910 (w), 2790 (m), 2610 (m), 2510 (w), 1775 (m), 1720 1700 (vs), 1605 (w), 1580 (s), 1485 (s), 1455 (vs), 1400 (s), 1325 (w), 1300 (m), 1280 (w), 1260 (vs), 1210 (w), 1125 (m), 1100 (m), 1080 (w), 890 (w), 860 (m), 810 (w), 790 (s), 750 (s), 730 (w), 700 (w), 675 (m) [cm^{-1}].

Synthesis of 3-(3,5-dioxo-1,2,4-triazolin-4-yl)benzoic acid

First 0.47 g (2.12 mmol) of the urazole are suspended in 150 ml ethyl acetate together with 8 g freshly dried Na_2SO_4. The mixture is cooled with ice while gaseous NO_2 is bubbled through the mixture for 15 min. When there is no further change in the red colour arising from the product, excess of NO_2 is removed by a stream of nitrogen. After filtration the solvent is removed under vacuum.

Yield: 0.4 g (86%).

^1H n.m.r. (acetone-d_6): 7.8–8.2 ppm (m, aromat.).

I.r.: 3500 2400 (OH), 3080 (w), 2960 (w), 2820 (w), 2660 (m), 2560 (m), 1820 (w), 1760 (vs), 1680 (vs), 1600 (w), 1580 (m), 1520 (w), 1485 (m), 1460 (m), 1410 (m), 1390 (s), 1310 (s), 1270 (s), 1160 (s), 1100 (w), 1075 (w), 1030 (w), 1010 (w), 920 (m), 890 (m), 810 (m), 750 (m), 730 (s), 700 (w), 670 (s) [cm^{-1}].

Synthesis of 3-[1-(but-1-en-2-yl)-3,5-dioxo-1,2,4-triazolidin-4-yl]benzoic acid

First 100 ml of methylene chloride are cooled in a three-necked round-bottom flask to −70 C. *Trans*-2-butene is bubbled through the solvent until saturation. Then 0.4 g of **3** dissolved in 30 ml ethyl acetate are slowly added. The red colour disappears rapidly. After stirring for another 15 min the solvent and excess butene are removed under vacuum. The raw product is recrystallized from THF/water (1:1).

Yield: quantitative (with respect to the raw product).

M.p.: 208 C (decomposition).

Elemental analysis: C, 56.23 (56.72); H, 4.91 (4.76); N, 14.71 (15.27).

^1H n.m.r. (acetone-d_6): 1.5 ppm (3H, d, CH_3); 4.8 ppm (1H, q, =CH–) 5.3 ppm (2H, m, $=CH_2$); 6.0 ppm (2H, m, NH and CH N); 7.5–8.1 (3H, m, aromat.); 8.3 (1H, s, aromat.).

I.r. (KBr): 3600–2300 (OH), 3420 (w), 3140 (m), 3060 (m), 2960 (m), 2910 (m), 2840 (w), 2650 (m), 2600 (m), 2540 (m), 1710 (s), 1700 1680 (vs), 1600 (w), 1580 (s), 1480 (s), 1450 (s), 1410 (s), 1310 (s), 1280 (m), 1250 (s), 1160 (m), 1140 (m), 1120 (w), 1080 (m), 1060 (w), 1020 (w), 990 (w), 970 (w), 935 (s), 910 (w), 825 (s), 760 (s), 720 (s), 660 (m), 640 (m) [cm^{-1}].

Other materials and reactions

4-Phenyl-1,2,4-triazoline-3,5-dione was prepared according to literature prescriptions[6]. The synthesis of **2** and its polymer analogous reaction is described in a former part of this series[2].

The polymer analogous reaction with polybutadiene is carried out in the usual manner at room temperature. Various amounts of **2** or **3** dissolved in THF are added to a THF solution of the polybutadiene. Termination of the reaction is indicated by the complete disappearance of the red colour of the triazolinediones. After stirring for another 30 min the solutions were filtered and films were cast. After most of the solvent had evaporated the films were dried until constant weight under reduced pressure.

The polybutadienes were either *cis*-1,4-polybutadiene (CB-10, supplied by Hüls AG, $M_n = 200\,000$, $M_w/M_n = 2$) or a PB made by anionic polymerization ('PB-10',

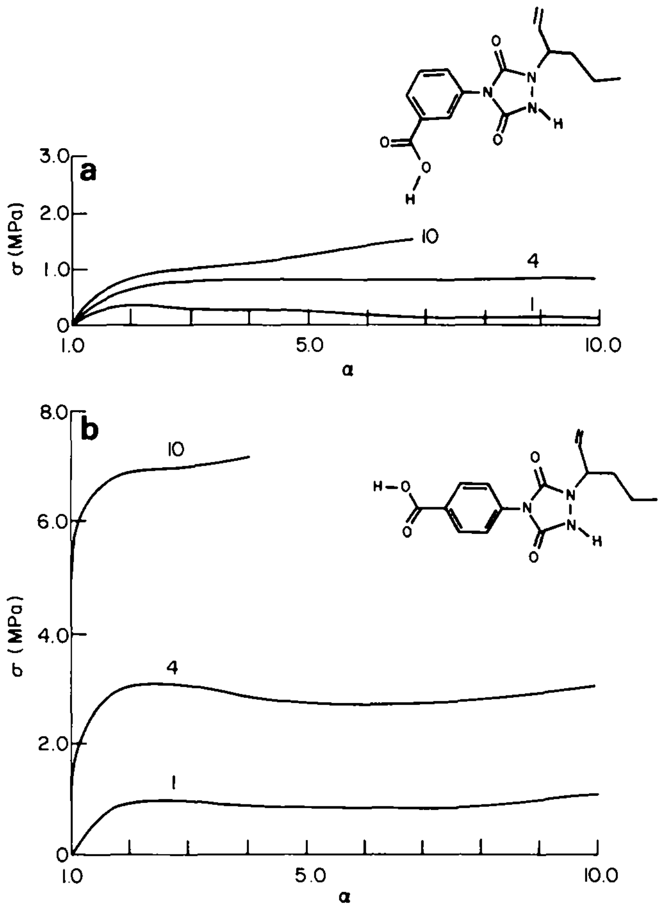

Figure 1 (a) Stress–strain curve of CB-10 modified with **3**. Concentrations as indicated. (b) Stress–strain curves of CB-10 modified with **2**

n-BuLi, cyclohexane, $M_n = 10000$, $M_w/M_n = 1.04$). For the mechanical and SAXS experiments the high-molecular-weight CB-10 was used, while the d.s.c. and i.r. investigations were performed on modified PB-10 samples.

Experimental set-ups

Stress–strain curves were obtained using an Instron 1120 tensile tester. Strips of 40 mm length, 8 mm width and about 0.35 mm thickness were cut from the films. The measurements were performed at room temperature, at a strain rate of 20 mm min^{-1}. Similar strips were used in a Kratky camera for SAXS investigations. The i.r. spectra were obtained on a Bruker IFS48 *FT*i.r. spectrometer. Films were cast from THF solutions on KBr pellets. The molecular modelling calculations were made using the PC model program by Serena software. Starting from the minimized conformation it is possible to calculate an energy profile of the rotation around a given bond. Only van der Waals interactions are taken into account in this calculation.

RESULTS AND DISCUSSION

Synthesis

Synthesis of **3** is performed in analogy to **2**. Starting from 3-aminobenzoic acid ethyl ester, the 3-carboxyethyl ester phenylisocyanate is prepared by phosgenation with triphosgene. The isocyanate is reacted with ethyl carbazate to the 1-(ethoxycarbonyl)-3-ethoxycarbonylphenylsemicarbazide. Ring closure is accomplished starting from the semicarbazide using aqueous sodium hydroxide. The benzoic acid ester is directly hydrolysed in the reaction medium and 4-(3′-carboxyphenyl)-1,2,4-triazolidine-3,5-dione is obtained. NO_2 in ethyl acetate is used for the oxidation to the reactive 1,2,4-triazoline-3,5-diones (**3**). The stability of the new triazolinedione **3** in solution was checked by observing the u.v. extinction at 524 nm. Although triazolinediones are known to be unstable in the presence of acids, **3** just decomposes to about 3% within 12 h in ethyl acetate solution, comparable to the stability of **2**. This means that it is possible to handle these reactive heterocycles for sufficient time. For further characterization the addition product of **3** with *trans*-2-butene was synthesized (see Experimental).

Stress–strain behaviour

The macroscopic properties of CB-10 carrying various amounts of the different functional groups were tested by stress–strain experiments. In *Figure 1a* the stress–strain curves are shown for CB-10 modified with **3**, and for comparison curves of CB-10 modified with **2** (*Figure 1b*). The materials are highly deformable and the stresses increase with increasing degree of modification in both cases. Nevertheless the two isomers **2** and **3** show a very different mechanical behaviour. The shapes of the curves of the *para* derivative (PB-U4A) are quite different from those of PB-U3A. In addition there are strong differences in the values of the stress at given strains. The PB-U4A samples show much higher stresses.

The samples of the PB-U4A series show a yield-type behaviour at certain elongation ratios. This behaviour has been explained qualitatively with a partial disruption of the supramolecular structure[2,7]. In the stress–strain curves of PB-U3A such a yielding behaviour is not observed at all. The similarity of PB-U4A to multiblock copolymers becomes more evident in *Figure 2*, where the results of cyclic stress–strain experiments are shown, in which the elongation ratio α was increased in each subsequent stretching cycle. The material shows strain softening behaviour. *Figure 3* shows the results of the same experiment performed on a CB-10 modified with 4 mol% of **3**. There is no indication for strain softening in this case.

In *Figure 4* the Young's modulus obtained from the initial slope of the stress–strain curves is plotted as a function of the degree of substitution for the polybutadienes modified with the different agents. While the modulus strongly increases with the degree of modification

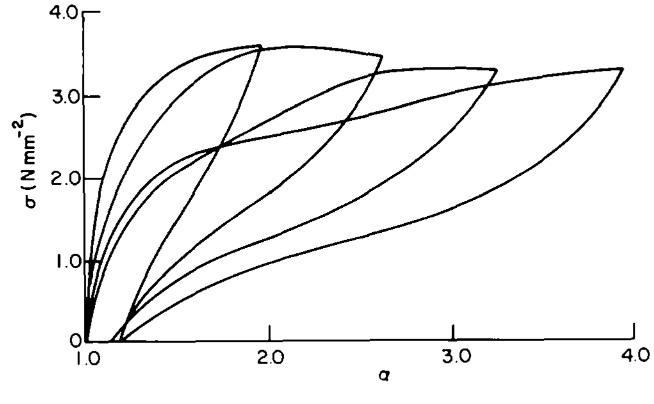

Figure 2 Cyclic stress–strain curves of CB-10 modified with 4% of **2**. The maximum of the ratio of elongation is increased by 1 after each cycle

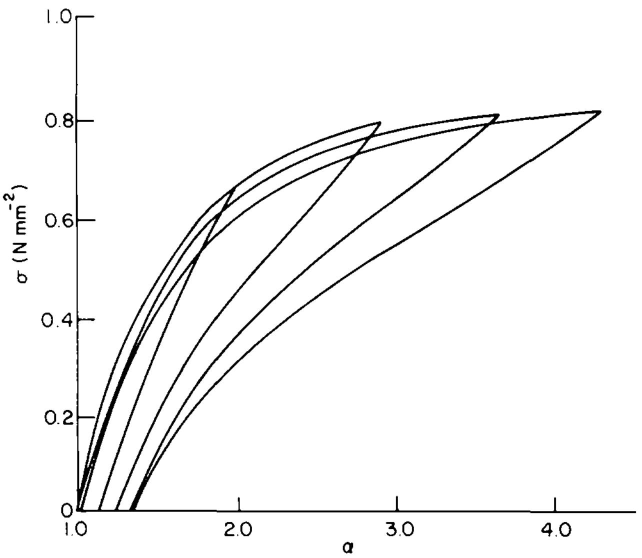

Figure 3 Cyclic stress–strain curves of CB-10 modified with 4% of **3**. Same conditions as in *Figure 2*

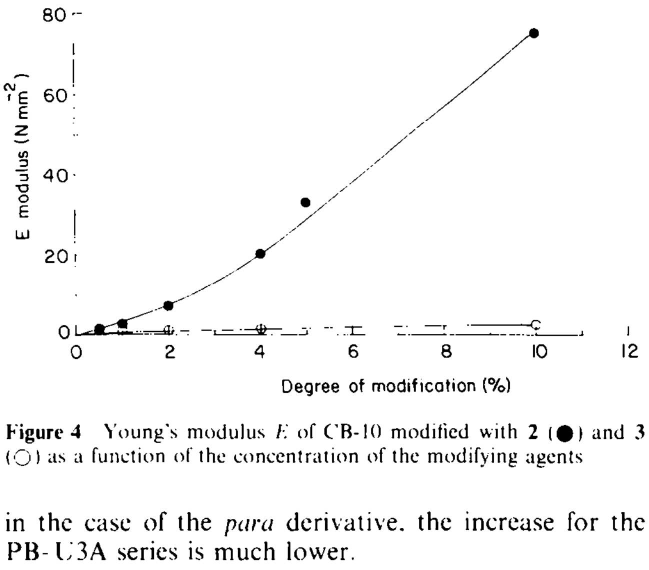

Figure 4 Young's modulus *E* of CB-10 modified with **2** (●) and **3** (○) as a function of the concentration of the modifying agents

in the case of the *para* derivative, the increase for the PB-U3A series is much lower.

Nevertheless the carboxy group has an additional crosslinking effect. This is shown in *Figure 5* where stress strain curves of CB-10 modified with 2 mol% of **1**, **2** and **3** are shown for comparison. The stress level is higher for PB U3A compared to the CB-10 modified with monofunctional groups, but still much lower than in PB U3A samples.

Other findings

Other methods that proved supramolecular structure formation in the case of PB U4A were performed on PB modified with the *meta* isomer **3**. The already mentioned 'melting' endotherm at about 80°C observed in polybutadienes modified with **2** is one of the most important findings indicating supramolecular structure formation. The enthalpy and the temperature of the transition depend on the concentration of functional groups[8]. The effect is attributed to an order–disorder transition. Isolated hydrogen-bond complexes do not show a cooperative transition from bonded to free species at a distinct temperature. Thus this melting must be correlated with a break-up of aggregates, formed by the association polymers.

In samples of polybutadiene modified with various amounts of the *meta* isomer **3** there appears no calorimetric transition other than the glass transition.

(i) In first experiments we were not able to detect a temperature-dependent scattering maximum in the SAXS experiment in polybutadienes modified with **3**. In the case of the *para* isomer a scattering maximum at low angles indicates phase separation between the aggregates of association polymers and the PB matrix[1,8].

(ii) It is known from temperature-dependent *FT*i.r. spectra of the PB–U4A series that some absorption bands in the carbonyl stretching region cannot be attributed to simple hydrogen-bonded dimers of acid and the urazole groups. Especially the band at about 1755 cm^{-1} present in the spectra of PB–U4A below the transition temperature does not exist in the i.r. spectrum of PB carrying the *meta* isomer (*Figure 6*). In the room-temperature i.r. spectrum of PB U3A the strong and broad band at about 1700 cm^{-1} is probably the superposition of the absorption bands of carboxy and urazole dimers. Temperature-dependent spectra just indicate a shift of thermodynamic equilibrium towards more uncomplexed species.

Molecular model calculations

MMX calculations were performed on models of ene reaction addition products of **2** and **3**. According to the minimized conformation both the urazole and the aromatic ring are planar. The dihedral angle between these cycles is calculated to be about 45°. The angular

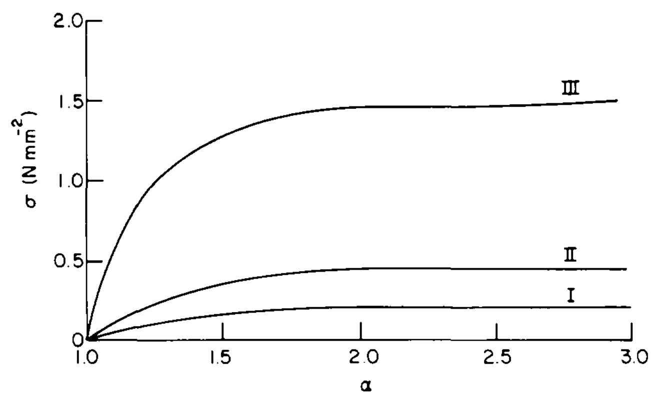

Figure 5 Stress–strain curves of CB-10 modified with **1** (curve I), **2** (curve III) and **3** (curve II) (2 mol%)

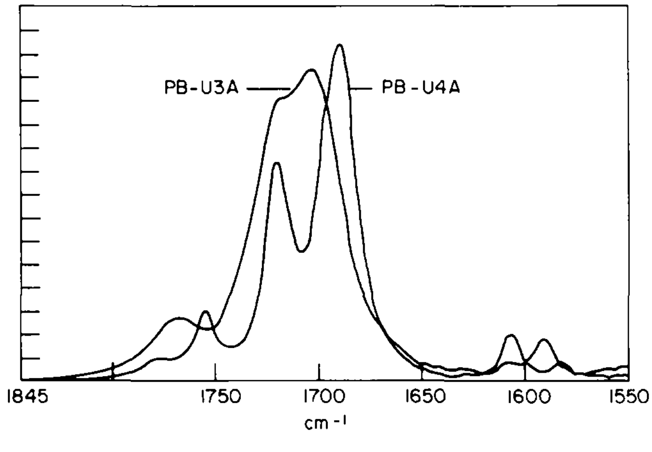

Figure 6 Room-temperature i.r. spectra of PB-10 modified with 1 mol% of **2** and of **3** as indicated

dependence of the potential energy curve shows a distinct maximum at 0° when heterocycle and aromatic ring are coplanar (*Figure 7*). The calculated height of the potential energy barrier is about 23 kcal mol^{-1}, which is large enough to suppress, or at least reduce drastically, the rotation around the nitrogen–carbon bond that connects the heterocycle and the aromatic ring at room temperature. The origin of this high energy barrier is the repulsive interactions between the oxygen atoms of the urazole ring and the hydrogens in the *ortho* position.

The calculated conformation results of the addition product of **2** with *trans*-2-butene is in amazingly good agreement with a single-crystal structure analysis of this molecule. The calculated dihedral angle is nearly exactly that found in the single crystal[5].

In addition to the calculations concerning the structure of the single molecule we were interested in the estimation of the strength of the hydrogen bond between urazole and acid groups. For all types of possible contacts (urazole–urazole, urazole–acid, acid–acid) the calculations result in a lower total energy compared to the isolated units. Energies of the hydrogen bonds are calculated to be nearly the same for dimers of the acid and for dimers of the urazole for the *meta* and the *para* derivative (calculated to be about 9–10 kcal mol^{-1} dimer). A similar value is obtained for the bond energy of a urazole acid contact. Thus these calculations do not rule out such contacts.

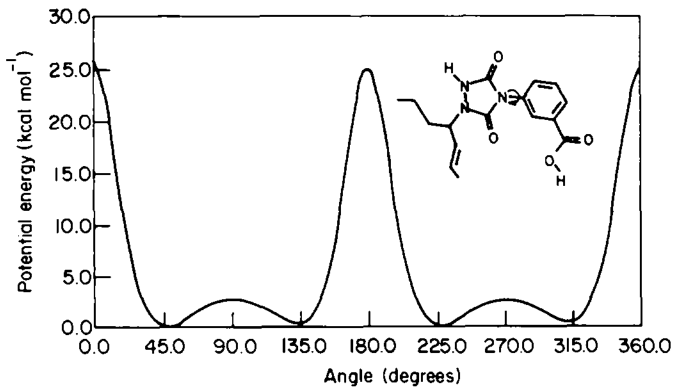

Figure 7 Calculated potential energy for the rotation of the aromatic ring around the nitrogen–carbon bond for a model of an addition product of **3**. The minimum corresponds to a dihedral angle between the aromatic and the heterocyclic ring of about 45°

Discussion

The presented experimental data show a very different behaviour of polybutadiene modified with **2** (*para*) or **3** (*meta*).

The differences in the room-temperature i.r. spectra reflect a different organization on the molecular level. The i.r. absorption bands related to supramolecular ordering of PB–U4A below the transition temperature are missing in the spectrum of PB–U3A at any temperature. Furthermore there is only little change in the spectra on increasing the temperature compared to PB–U4A where structural changes are clearly seen in the spectra. Moreover the i.r. spectra of PB–U3A resemble that of PB modified with monofunctional **1**. In the latter case an equilibrium between hydrogen-bonded and free urazole groups can clearly be identified[9].

The different states of molecular ordering of the polar groups are reflected in the mechanical properties of the polybutadienes modified with the different triazolinediones. Polybutadienes modified with **2** show high moduli and a yield behaviour, both indicating effective physical crosslinking. From SAXS and i.r. dichroism measurements under elongation the stress-strain behaviour could be attributed to an orientation of the

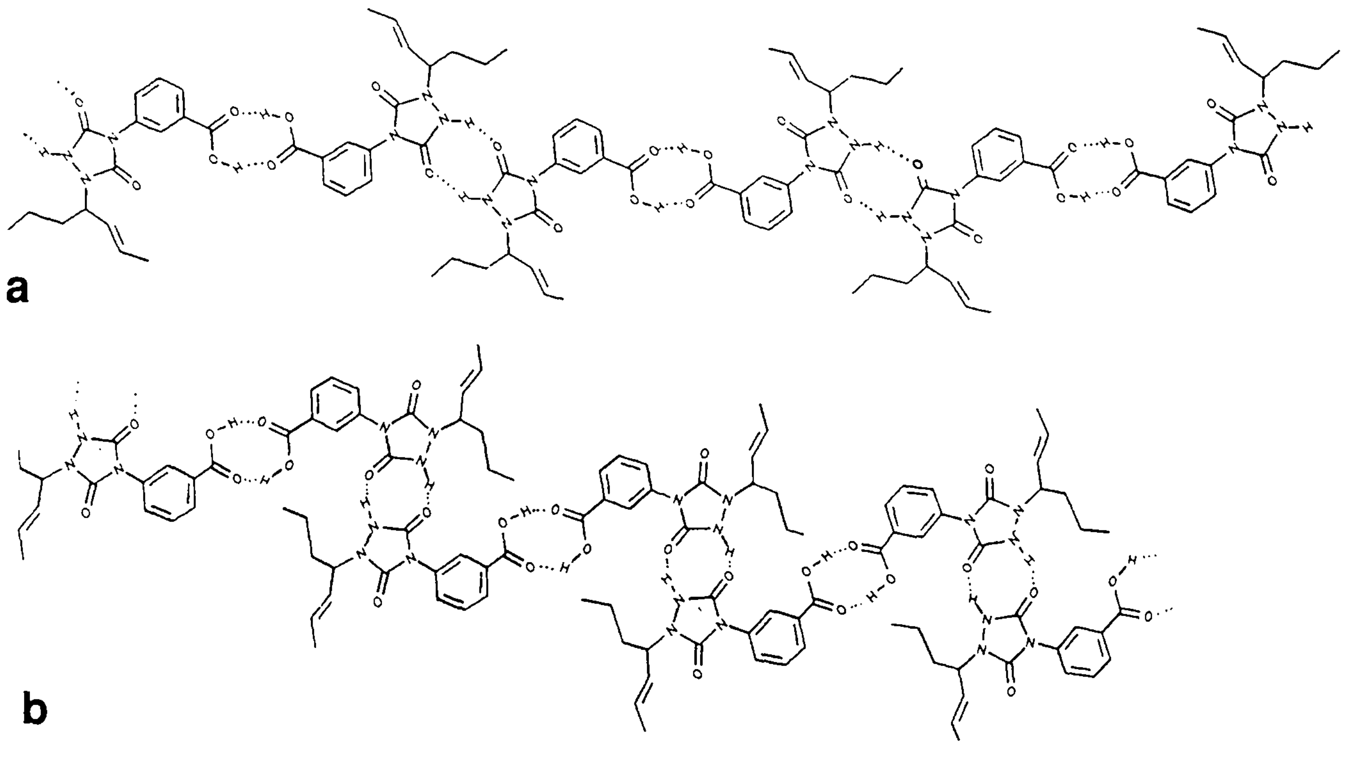

Figure 8 Schematic (two-dimensional) representation of association polymers formed by 3-carboxyphenylurazole groups of different stereochemistry (a and b)

aggregated association chains followed by partial disruption of the oriented junction zones[10]. In contrast to these findings the mechanical behaviour of PB–U3A resembles that of PB modified with **1**. In the latter case it is well known that isolated binary hydrogen-bond complexes are responsible for the formation of a physical network. In contrast to PB–U4A there is no further stabilization of the hydrogen bonds so that a continuous transition to flow occurs with increasing temperatures.

The fact that the simple change of the carboxy group from *para* to *meta* position results in materials with quite different properties is a consequence of the unusual supramolecular organization of the polar groups in PB–U4A. As can be seen from the experimental findings the architecture of the functional groups has a prominent influence on structure formation in analogy to biological systems. The individual hydrogen-bond complexes of the *meta* derivative are expected to have a strength similar to those formed by the *para* derivative. The pK_a of the carboxy groups might be different in the two isomers owing to the different electronic effects of the heterocycle. Therefore it might be possible that hydrogen bonding occurs between the urazole and the acid group in the case of the *meta* derivative, whereas acid–acid and urazole–urazole complexes are favoured by PB–U4A moieties.

Nevertheless the formation of an association polymer by the two functional sites is possible in either case. In *Figure 8* linear association polymers of PB–U3A groups are shown schematically. This picture gives a two-dimensional representation of chains of the two possible stereoisomers resulting from the hindered rotation. These stereoisomers are enantiotopic with respect to each other. Owing to the height of the rotational barrier for the C–N bond between the aromatic ring and the heterocycle the two isomers are not able to transfer into one another at room temperature. An association polymer formed by these different groups is expected to become very irregular. If urazole acid contacts are the main structural motifs in the addition products of **3** with PB an association polymer would show similar irregularities.

The differences in the resulting properties of the *meta* and *para* substituted derivatives can easily be explained in terms of these irregularities of the association polymers. Furthermore it can be concluded that specific interactions between the different strands are responsible for the lateral aggregation in the PB–U4A samples, i.e. that the aggregation is not just due to thermodynamic phase separation between the polymer matrix and the association polymer of 4-carboxyphenylurazole groups.

From the experimental findings we conclude that in polybutadiene modified with **3** the principles of structure formation are similar to those carrying monofunctional phenylurazole groups. Although the additional site for hydrogen bonding (the carboxy function) is involved in complex formation, the dynamics of the single hydrogen bond has the determining effect on the resulting properties.

With these results our model of cooperative structure formation of the 4-carboxyphenylurazole moieties in non-polar polybutadiene matrix gains further support.

ACKNOWLEDGEMENT

Financial support by the DFG through the Gerhard Hess grant for R.S. is gratefully acknowledged.

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