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Cooperative Structure Formation by Directed Noncovalent Interactions in an Unpolar Polymer Matrix. 7. Differential Scanning Calorimetry and Small-Angle X-ray Scattering[†]

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ABSTRACT: 4-Urazoylbenzoic acid groups which are attached randomly to flexible 1,4-polybutadienes form ordered supramolecular domains via hydrogen bonds and dipole–dipole interactions. The influence of the backbone molecular weight on the degree of supramolecular ordering is studied by differential scanning calorimetry (DSC) and small-angle X-ray scattering (SAXS). The ordered domains formed by the functional groups are phase separated from the amorphous polymer matrix, giving rise to a maximum in the small-angle X-ray scattering. From the enthalpy change associated with the order–disorder transition and the SAXS data the dimensions of the ordered supramolecular domains are estimated. The number of polar groups incorporated into a single ordered domain is in the range of 20–90. Between 5 and 20 units form a single association chain.

I. Introduction

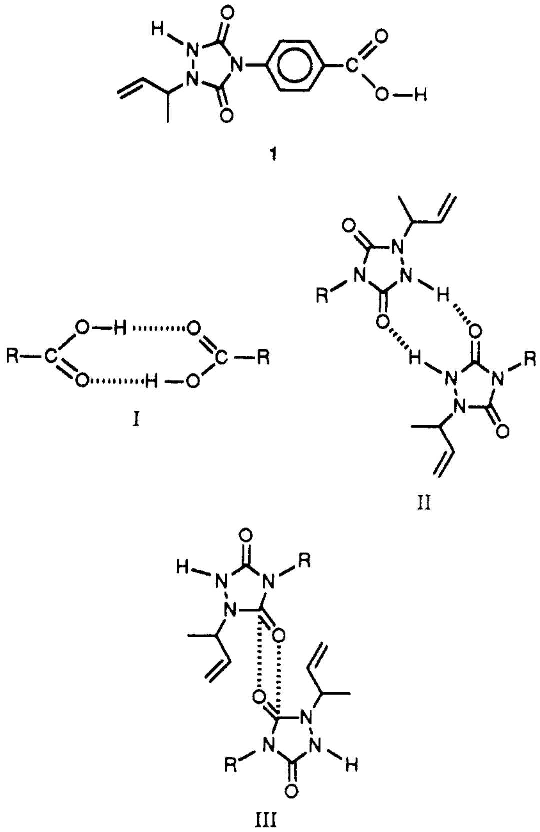
The formation of ordered supramolecular structures by hydrogen bonding has received increasing interest in low molecular weight chemistry.[1-4] The growing understanding of the principles controlling secondary interactions has already led to the prediction and realization of various supramolecular structures via suitable design of the functional groups.[3,4] Such systems are of interest not only as model compounds for supramolecular structure formation in biological systems but also as tools to create new materials exhibiting special properties.[5]

As a characteristic of such compounds, supramolecular order is achieved by a self-assembling process due to directed noncovalent interactions. Supramolecular self-assembly is not restricted to low molar mass crystals but may also occur and be useful in polymeric systems. Recently[6] we have reported on a new type of supramolecular self-assembly in 4-(1-but-1-en-3-yl-3′,5′-dioxo-1′,2′,4′-triazolidin-4-yl)benzoic acid (1 in Chart I): Three different types of noncovalent interactions form a two-dimensional array from these molecular units: I, hydrogen bonds between two carboxylic acid groups; II, hydrogen bonds between two urazoyl units; III, a unique dipole–dipole interaction between the carbonyl groups of the urazole heterocycle which are not involved in hydrogen bonding.

The structure can be regarded as an association polymer, formed by alternating urazole–urazole (U–U) and acid–acid (A–A) hydrogen bonds (Figure 1a), linked together by the dipole–dipole interactions into a two-dimensional lattice (Figure 1b).

These 4-urazoylbenzoic acid groups (1) can also be attached to polydienes via a polymer analogous reaction of the corresponding triazolinedione with a polydiene. The reaction of triazolinediones with polydienes is quantitative, if the degree of modification is kept below 50 mol % and occurs within minutes at room temperature.[7]

Chart I



In previous publications the influence of 4-phenylurazole groups on the properties of lightly modified polybutadiene has been described in detail.[8-10] In the case of 4-phenylurazole, the polar units form binary complexes via hydrogen bonds (II) but no extended junction zones. From biological networks it is known that extended junction zones are necessary to stabilize reversible networks. Extended junction zones via hydrogen bonds in modified polybutadienes can be realized by attaching additional functional groups to the urazoyl unit.[11,12] However, only when 4-urazoylbenzoic acid groups 1 (U4A) were attached to polybutadiene, the material properties indicated the formation of highly ordered extended junction zones.[13-16]

Differential scanning calorimetry of a modified polybutadiene carrying 4 mol % of 1 has provided first experimental evidence for the formation of an ordered supramolecular structure of the polar groups in the

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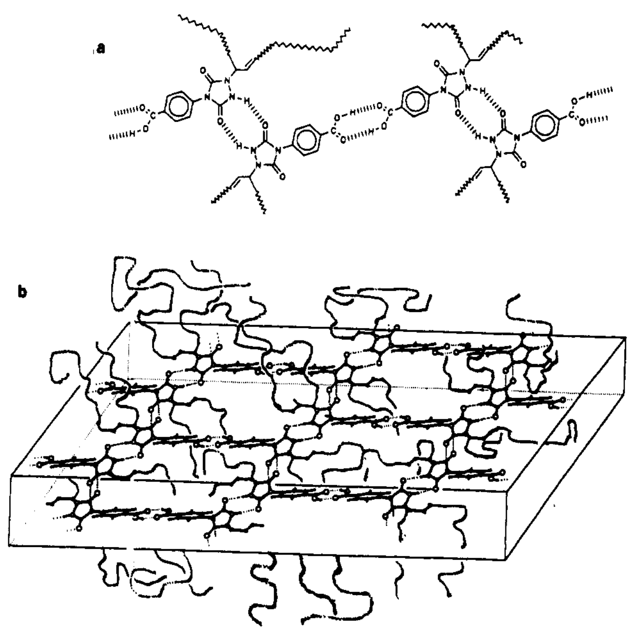

Figure 1. (a) Association chain of 4-urazoylbenzoic acid groups, attached to polybutadiene. (b) Two-dimensional structure of urazoylbenzoic acid groups. Arrangement of the functional groups according to the single crystal structure of a low molecular weight model compound.[6] In the case of attaching the groups to the polybutadiene, the polybutadiene chains emerge from the top and from the bottom.

polymer melt.[13] On heating, the modified polybutadiene carrying one functional group at every 25th repeating unit (on average), an endothermic transition at about 80 °C is observed by differential scanning calorimetry (DSC). The glass transition temperature was only raised for about 5 deg with respect to the unmodified polybutadiene. In first small-angle X-ray scattering (SAXS) experiments of a technical-grade polybutadiene functionalized with 1 a scattering maximum at small angles was observed.[13] Originally, the observation of a small-angle X-ray scattering maximum was rather surprising, because no heavy atoms are present in this statistical copolymer system, contrary to ionenes or ionomers. Upon uniaxial stretching strong orientation of the scattering units parallel to the stretching direction was indicated from the SAXS pattern. The maximum in the SAXS has been interpreted as the result of a microphase separation between the unpolar polymer matrix and the ordered supramolecular structure of the functional groups. The endothermic transition of the DSC heating trace was considered as an order–disorder transition of the aggregate of polar groups.[13,14,16]

On the basis of these results and further experimental evidence resulting from temperature-dependent IR measurements,[17] dynamic mechanical properties,[15] stress–strain properties,[14] and IR dichroism studies,[18,19] we proposed the model given in Figure 2.[13] The difunctional urazoylbenzoic acid groups 1 form linear association chains by hydrogen bonding (Figure 1a). However, the formation of such an association chain cannot explain a "melting" as observed by DSC. Thus further aggregation of the (preformed) association chains to extended ordered structures of the functional groups in the polymer matrix must occur. This additional aggregation, which could be attributed to the dipole–dipole interaction,[6,17,19] causes a cooperative stabilization of the hydrogen-bond complexes. The transition at relatively high temperatures can therefore be explained with the breakup of the "polymer-bound" supramolecular structure.

In this paper we will report the results of temperature-dependent SAXS and DSC experiments that give further information on the supramolecular structure of the polymer-bound functional groups. The influence of a varying concentration of functional groups and the influence of the molecular weight of the polymer backbone will be discussed. As a final goal we attempt to obtain information about the size of the supramolecularly ordered domains.

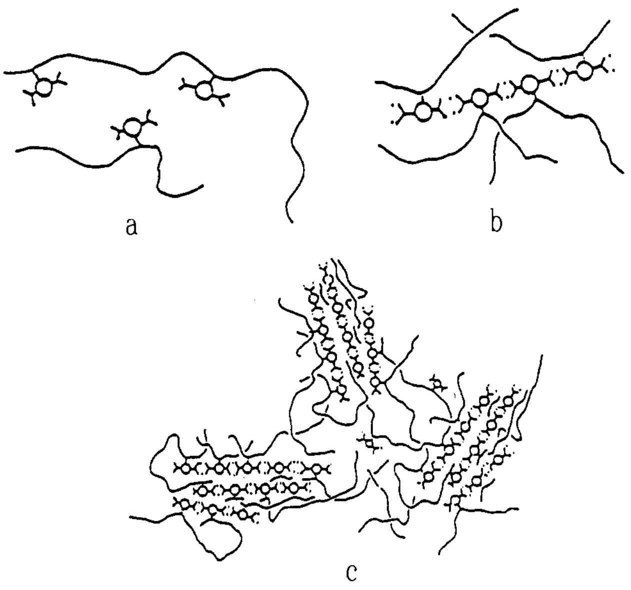

Figure 2. Schematic picture of the aggregation of linear association polymers, formed by difunctional groups attached to a covalent polymer (a→b), into ordered supramolecular domains (b→c), dispersed in the matrix of flexible covalent chains (according to ref 13).

Table I
Characterization of Unmodified Polybutadienes

sample	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	microstructure
PB-10	16 200	1.02	portion 1,4 >96%
PB-30	31 000	1.02	portion 1,4 >96%
CB10	200 000	2.0	portion cis 95%

II. Experimental Section

Sample Preparation. The unmodified polymers used in this study were either prepared in this laboratory using standard anionic techniques (initiator, s-BuLi; solvent, cyclohexane; room temperature) or technical-grade high *cis*-1,4-polybutadiene (CB10 Hüls AG). The characterization of the starting materials is given in Table I.

The synthesis of the modifying agent 2 [4-(3,5-dioxo-1,2,4-triazolin-4-yl)benzoic acid] and its polymer analogous reaction with polybutadiene has been described elsewhere.[14] Samples with different concentrations of functional groups were prepared by reacting the unmodified polybutadiene with the appropriate amount of the modifying agent. Freshly prepared 2 has always been used. Stability of the highly reactive triazolinedione has been checked by UV spectroscopy.[22] A typical experimental procedure is as follows: 2 g of polybutadiene is dissolved in THF or toluene (5% w/v). The appropriate amount of 2 is dissolved in ethyl acetate and added to the polybutadiene solution under vigorous stirring. The red color of 2 vanishes after about 10 min (much faster in toluene than in THF). The reaction mixture is stirred for 2 h more. After this time, 0.2 wt % of antioxidant (2,6-di-*tert*-butyl-4-methylphenol) was added to the solution. Films were cast either directly from this solution or after precipitation and redissolution in dried, peroxide-free THF. Films were cast in flat-bottomed Petri dishes. Samples for DSC always were precipitated in methanol before casted at films. All samples were dried in vacuum at room temperature and stored in the refrigerator.

The concentration of functional groups in the modified polymers is given in mole percent with respect to the repeating

Table II
Designation and Thermal Characterization of Modified Polybutadienes[a]

sample	degree of modification mol %	degree of modification wt %	no. of groups per chain (with respect to $\bar{M}_n$)	T_g, °C	T_m, °C	ΔH, J g^{-1}	ΔH, kJ mol^{-1}	f_{ura} ±0.05%
SQ-U4A	16.6	34.7	1		89		15.27	1.00
PB-10-U4A-0.5	0.5	2	1.5	−100	62	0.82	9.1	0.60
PB-10-U4A-1	1.0	4	3	−99	67	2.19	12.3	0.80
PB-10-U4A-2	2.0	7.5	6	−96	75.4	5.53	14.2	0.92
PB-10-U4A-3	3.0	10.8	9	−97	80.7	6.66	13.5	0.88
PB-10-U4A-4	4.0	14.0	12	−93	81	8.72	13.7	0.86
PB-10-U4A-4.5	4.5	15.5	13.5	−94	81.9	9.11	12.9	0.84
PB-10-U4A-7.5	7.5	23.3	22.5	−87	83.9	12.35	11.6	0.76
PB-10-U4A-10	10	28.8	30	−82	84.9	10.71	8.1	0.53
PB-10-U4A-15	15	37.8	45		69.1	6.77	3.9	0.25
PB-10-U4A-20	20	44.7	60		78.2	8.52	4.2	0.28
PB-30-U4A-0.5	0.5	2	2.8		66.8	0.27	3.0	0.20
PB-30-U4A-1	1	4	5.7		70.6	1.42	8.0	0.52
PB-30-U4A-2	2	7.5	11.4		72.4	2.86	8.4	0.55
PB-30-U4A-4	4	14.0	23		79.3	6.17	9.7	0.63
CB10-U4A-1	1	2	37		nd	nd	nd	
CB10-U4A-2	2	4	74		nd	nd	nd	
CB10-U4A-4	4	7.5	150		73.2	1.78	2.8	0.19
CB10-U4A-10	10	28.8	370		79.9	7.9	6.0	0.39

[a] nd = too broad to be determined.

units of the polybutadiene. A degree of substitution of 4 mol % corresponds to one functional group every 25th repeating unit. The polymer analogous reaction of polydienes with 3,5-dioxo-1,2,4-triazolines results in a statistical modification.[7] If the degree of polymerization is much larger than the average number of functional groups per chain and the reaction occurs in homogeneous solution, the distribution of functional groups obeys the conditions of a Poisson distribution for polydienes of narrow molar mass distribution; i.e., every polymer chain contains the same number of functional groups.[23] Sample designation and characterization of the substituted polybutadienes is given in Table II.

A low molecular weight model compound of similar structure has been prepared by reacting **2** with a large excess of squalene to avoid multiple substitution: 18 g (43.8 mmol = 263 mmol of double bonds) of squalene is dissolved in 50 mL of dry ethyl acetate. A total of 1.04 g (4.74 mmol) of **2**, dissolved in 50 mL of ethyl acetate, is added under stirring. After disappearance of the red color, the solvent was removed in vacuum. An excess of unreacted squalene was removed by repeated extraction of the reaction mixture with petroleum ether (bp 60–80 °C). No remaining unreacted squalene could be detected by thin-layer chromatography after this purification.

The degree of substitution of modified squalene (as compared to the polybutadienes) is 16.6 mol % (1 double bond out of 6 is substituted). A more detailed characterization of the squalene model compound SQ-U4A is given in ref 16.

Methods. Differential scanning calorimetry was performed on a DSC 7 (Perkin-Elmer) with TAS 7 software (Perkin-Elmer). The instrument was calibrated using standard calibration procedures (indium). Glass transitions were measured at a heating rate of 20 K/min, taking the inflection point of the heat capacity change as the T_g. For analysis according to the one-dimensional Ising model (see below), absolute values of the heat capacity are measured by the DSC 7. For this purpose the instrument was calibrated with Al_2O_3 according to standard procedures. The heating rate was 40 K/min. Due to the small heats of transition these relatively high heating rates are necessary to allow quantitative evaluation of the enthalpies. Lower heating rates give the same values of the transition temperature (within experimental errors). Pretreatment of the samples was essential to obtain reproducible results: the samples were first heated in the aluminum pans to temperatures above the order–disorder transition and were stored at room temperature for several weeks to ensure complete structural relaxation and good thermal contact with the aluminum pan.[24]

Small-Angle X-ray Scattering. Temperature-dependent SAXS studies were made using a Kratky camera equipped with a variable-temperature cell using a one-dimensional position-sensitive detector (MBraun). The measurements were performed at MPI für Polymerforschung (Mainz). Technical assistance of MPI (group of Prof. Fischer) is gratefully acknowledged. The sample detector distance was 24 cm, and the width of the entrance slit was 80 μm. Ni-filtered Cu Kα radiation (λ = 0.154 nm) from an anode operated with 30 kV and 35 mA was used. The samples for the SAXS investigations were cut from cast films. Measurements were made at 30, 70, 80, 95, and 120 °C. The exposure time at each temperature was 30 min after temperature equilibration.

Absolute intensities were determined after correction of the data for detector "dead-time", parasitic scattering, and absorption of the sample. The data were desmeared according to the procedure of Strobl.[25] The scattering vectors **s** and **q** are defined as

$$\mathbf{s} = 2 \sin \Theta/\lambda \tag{1}$$

$$\mathbf{q} = 2\pi\cdot\mathbf{s} \tag{2}$$

As a first attempt the scattering data are analyzed according to a two-phase model.[26] For isotropic systems the scattering intensity at larger **q** values is given by Porod's law according to

$$\mathbf{I}(\mathbf{s}) = (\rho_{e1} - \rho_{e2})^2/8\pi^3 O\mathbf{s}^{-4} = K_p\mathbf{s}^{-4} \tag{3}$$

where $\rho_{e1} - \rho_{e2}$ corresponds to the electron density difference between the two phases.

For larger scattering vectors **s** the scattering intensity for point collimation is proportional to the internal surface O_s of the dispersed phase and to $\mathbf{s}^{-4}$ for point collimation. For slit-smeared data it follows that

$$\lim_{\mathbf{s}\to\infty} \mathbf{s}^3 I(\mathbf{s}) = K_p \tag{4}$$

This equation is valid for a system with sharp phase boundaries. Deviations from Porod's law are often interpreted in terms of a diffuse phase boundary. For this situation Ruland proposed the description of K_p according to

$$K_p = H^2(\mathbf{s})\, K_p' + I_b \tag{5}$$

where I_b is the background scattering and $H(\mathbf{s})$ describes the deviation from Porod's law. From a plot of $\mathbf{s}^3(I(\mathbf{s}) - I_b)$ versus $\mathbf{s}^2$ or ln $[\mathbf{s}^3(I(\mathbf{s}) - I_b)]$ versus $\mathbf{s}^2$ the deviation from Porod's law may be analyzed in terms of a phase boundary of finite thickness.[26]

The scattering invariant Q, defined as

$$Q = \int_0^\infty I_s(\mathbf{s})\, d\mathbf{s} \tag{6}$$

where I_s are the slit-smeared scattering intensities, is used to calculate the internal surface O_s (in units m^2/cm^3) at known volume fraction ϕ of one of the phases according to

$$O_s = 8\pi\phi(1-\phi)K_p \times 10^4 Q^{-1} \qquad (7)$$

This analysis of the data can be considered as a 0th-order approximation. No attempts will be made to derive the scattering function from a morphological model in analogy to the work done on ionomers,[27-29] which give a very similar SAXS pattern. Ongoing work will focus on this problem.[30]

III. Results and Discussion

Thermal Analysis. Glass Transition of Modified Polybutadienes (PB-10-U4A-*x* Series). Attaching urazole groups to polybutadiene increases the glass transition temperature.[7,31,32] The glass transition temperatures of the PB-10-U4A-*x* series obtained at a heating rate of 20 K min^{-1} are collected in Table II. Comparison of the glass transition temperatures of polybutadienes carrying either phenylurazole groups or the urazoylbenzoic acid groups shows that the increase of T_g is larger for polybutadienes carrying 4-phenylurazole groups,[31,32] which only forms dimeric hydrogen-bond complexes. While the T_g increase with respect to the unmodified polymer is 22 deg for a polybutadiene carrying 5 mol % of 4-phenylurazole groups (this corresponds to 14 wt %),[32] the glass transition of the polybutadiene carrying 5 mol % of 4-urazoylbenzoic acid groups (1) (this corresponds to 16.8 wt %) only increases for 5 deg. This already may be taken as a hint that the urazoylbenzoic acid groups are not distributed homogeneously in the polybutadiene matrix.

In polybutadienes modified with small amounts of 4-urazoylbenzoic acid the observation of an endothermic transition in the DSC heating trace was a key experiment, indicating the self-assembly of the functional groups to ordered supramolecular domains in the polymer melt though this transition seems similar to a crystalline melting its molecular nature must be different, because the domains of molecular order are necessarily strongly restricted, due to the fact that *two* polybutadiene chains emerge from every repeating unit. Thus the formation of a three-dimensional (micro)crystal is rather unlikely. In analogy to partially crystalline, multiphase polymer systems it can be expected that the "extent of order" in the modified polymer will be smaller than in corresponding low molecular weight model substances. The influence of the concentration of the functional groups on the supramolecular ordering is studied by varying the number of these groups for a given primary chain. Figure 3 shows the DSC traces of the PB-10-U4A-*x* series. The data are collected in Table II.

Even for the sample PB-10-U4A-0.5 (0.5 mol % substitution), with only about 1 functional group per chain, the endothermic transition is observed in the DSC heating trace. With increasing degree of substitution the "melting" temperature is shifted to higher values. At a heating rate of 40 K/min, the DSC peaks show a width of about 25–30 K.

Figure 4 shows the location of the maximum of the DSC traces for degrees of substitution up to 20 mol %. The dotted line corresponds to the transition measured for the low molecular weight model SQ-U4A under identical conditions. For very high degrees of substitution, i.e., 15 and 20 mol % (the traces are not shown in Figure 3), the transition becomes even broader and the maximum is shifted to lower temperatures.

To compare the effect of the concentration of functional groups on the transition enthalpy, the transition enthalpies obtained from the DSC experiments (in J g^{-1}) are recalculated to a molar basis, with respect to the concentration of polar groups (J mol^{-1}). The data are plotted in Figure 5 as a function of the degree of modification. Again the dotted line corresponds to SQ-U4A.

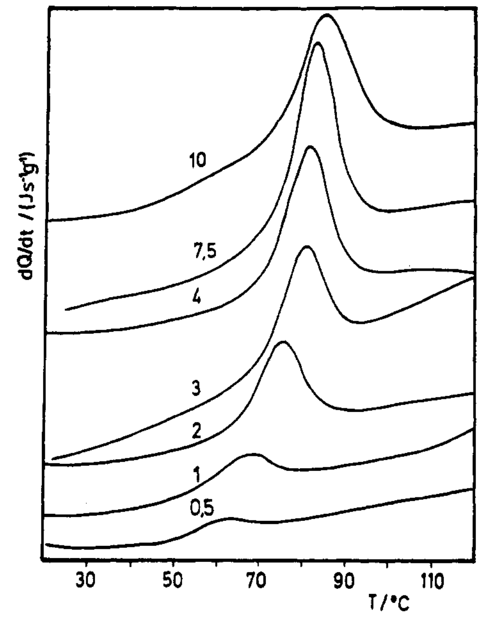

Figure 3. DSC heating traces of polybutadiene (PB-10) modified with different amounts of 4-(3,5-dioxo-1,2,4-triazolin-4-yl)benzoic acid (PB-10-U4A-*x* series). Numbers indicate the degree of functionalization.

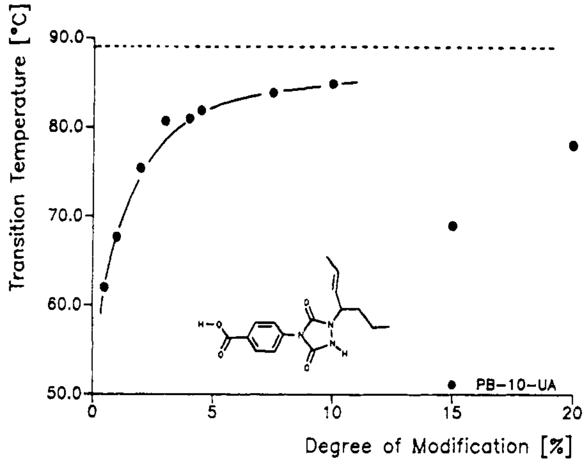

Figure 4. Temperatures of the maximum of the DSC heating traces of PB-10-U4A-*x* as a function of the degree of modification. The dotted line corresponds to modified squalene SQ-U4A.

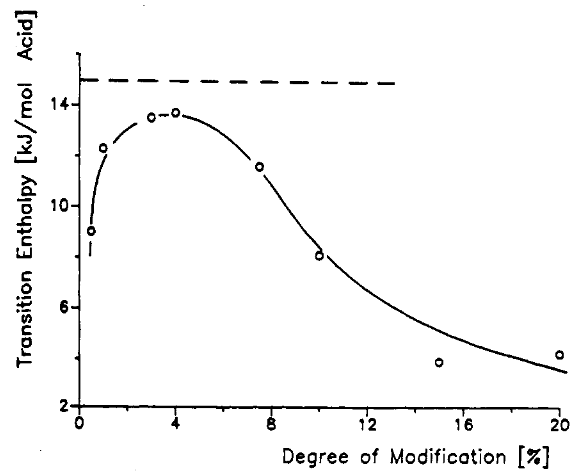

Figure 5. Transition enthalpy per mole of fucntional units of PB-10-U4A-*x*. The dashed line corrsponds to modified squalene SQ-U4A.

For low degrees of substitution (<4 mol %) the measured transition enthalpy per polar group increases and then passes through a maximum. At the maximum the value obtained for the substituted polybutadiene is about 90% of the value of SQ-U4A.

Increasing the annealing period at room temperature does not change the DSC transition. Thus is must be concluded that the observed behavior corresponds to the equilibrium with respect to self-assembling which can be reached for a given degree of substitution.

While the transition enthalpy (on a molar basis) has its maximum at about 4 mol %, the maximum in the transition temperature is at about 10 mol %. This difference indicates that the transition temperature and the transition enthalpy reflect different characteristics of the supramolecular ordering in these modified polybutadienes.

In analogy to the melting of partially crystalline polymers the transition temperature might reflect the size and/or the "perfection" of the ordered areas.[33] Thus the increase of the transition temperature with increasing substitution (degrees of modification <10 mol %) would correspond to an increasing size of the ordered domains. At higher concentrations of functional groups the ordered domains would not be able to approach the same degree of perfection anymore.

The concentration dependence of the transition enthalpy results from attaching a small number of groups to a high molecular weight chain molecule. At low concentrations of stickers (<4 mol %) the increase in the transition enthalpy with substitution indicates that the ordered domains grow in size or in number. This result is expected, if an equilibrium between "free" and "supramolecular ordered" functional groups is assumed. Increasing the concentration of polar groups increases the probability for a functional group to get incorporated into an ordered domain.

However, the decreasing value of ΔH (in J mol^{-1}) for higher degrees of substitution can only be explained by an increasing number of functional groups which are not incorporated into the ordered domains and thus do not contribute to the transition. This is an enthalpically unfavorable situation, because not all of the noncovalent interactions (e.g., hydrogen bonds and dipole–dipole interactions) are formed. Such a behavior can be readily explained by entropic restrictions caused by the polymer backbone.[23] If the value obtained for the squalene model is taken as the reference state, with all polar groups incorporated into ordered domains, we conclude that about 90% of the polar groups are in the ordered structure for PB-10-U4A-4, while this fraction is only 50% for PB-10-U4A-10. The remaining functional groups are distributed in the polybutadiene matrix, either uncomplexed, as binary U–U II or A–A I complexes or as association polymers which are not stabilized in an ordered domain. As a consequence the glass transition of the polybutadiene now increases more strongly. These considerations are based on the assumption that all groups are incorporated into the domain in the case of the squalene model.

Without considering effects of the surface energy of the ordered domains we assume that each functional group incorporated into the ordered structure contributes equally to the transition enthalpy. Thus the increase of the transition enthalpy at low degrees of modification can either result from an increase of the number of domains or an increase of the size of each single domain. Distinction between these two possibilities can be made from the SAXS experiments.

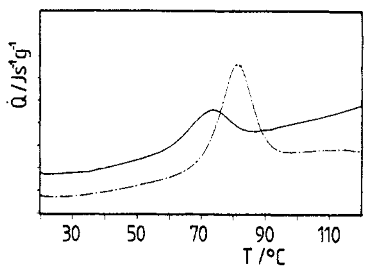

Figure 6. DSC traces of PB-10-U4A-4 (dot-dashed curve) and CB10-U4A-4 (solid curve). The heating rate was 40 K min^{-1}.

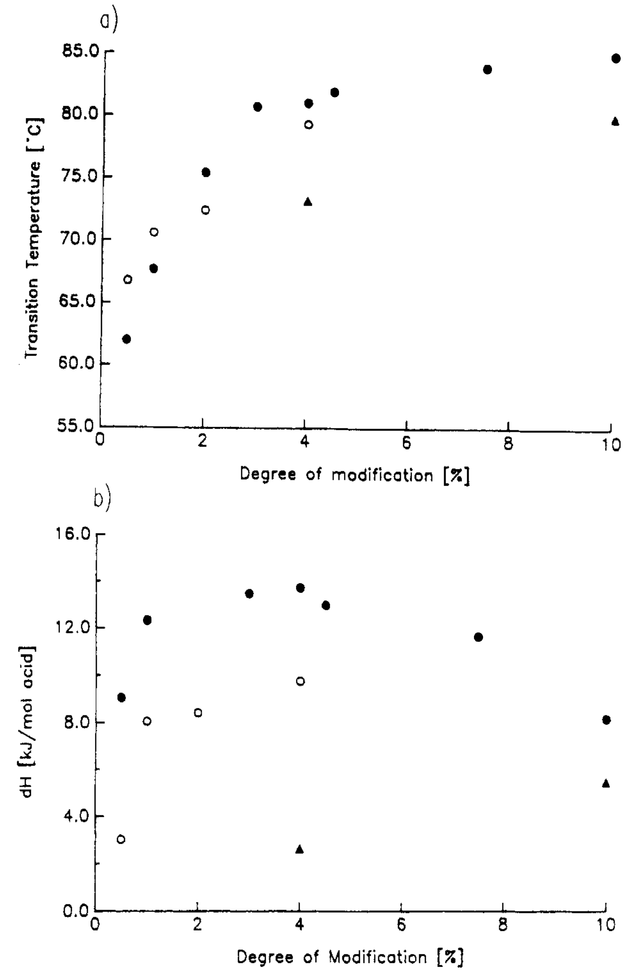

Figure 7. Temperatures of the maximum of the DSC heating traces of PB-10-U4A-*x* (●), PB-30-U4A-*x* (○), and CB10-U4A-*x* (▲) as a function of the degree of modification. (b) Transition enthalpy per mole of functional units of PB-10-U4A-*x* (●), PB-30-U4A-*x* (○), and CB10-U4A-*x* (▲) as a function of the degree of modification.

Influence of the Molecular Weight on the DSC Endotherm. Figure 6 compares the DSC traces of PB-10-U4A-4 with the high molecular weight CB10-U4A-4 at the same degree of substitution. Parts a and b of Figure 7 show the transition temperature and the transition enthalpies as a function of the degree of modification for degrees of modification <10 mol % for different molecular weights. It is evident from these data that the fraction of functional units incorporated in the ordered structure at a given degree of substitution decreases with increasing molecular weight of the polybutadiene. This reflects the increasing topological restrictions toward complex formation with increasing number of polar groups per chain—at the same overall concentration.

Magnitude and location of the DSC transition can be controlled also by simultaneous functionalization with 1 and monofunctional 4-phenylurazole.[16] From the dependence of the order–disorder transition on the stoichiometric ratio of di- and monofunctional associating sites we deduced the numbers of units incorporated in one association chain. Regarding the formation of the association polymer in analogy to a step reaction, we estimated that at a substitution of 4 mol % one association chain consists of about 10–15 urazoylbenzoic acid groups.

Analysis of the "Melting" Behavior in Analogy to the Helix–Coil Transition. Analysis of the temperature-dependent IR spectra shows that the melting is dominated by the disappearance of the absorption resulting from the dipole–dipole interaction but not by a sudden change of the fraction of hydrogen-bonded groups.[17,19] Thus the melting can be regarded as a cooperative breakdown of the interaction between the association chain polymers. Another attempt to estimate the length of the association chains involved in the structure formation may be based on the analogy of the present order–disorder transition with the helix–coil transition in biopolymers or biopolymer gels. The helix–coil transition can be treated according to the Zimm–Bragg model as a one-dimensional Ising problem.[34,35] This model describes a system as a two-state model. Whether a repeating unit is in an ordered (A) or disordered (B) state depends on the state of the neighboring units. Considering the transition of a chain of units in state AAAAAAA into a state BBBBBBB, a nucleating site BAAAAAA is generated first which then may grow. For a chain of 4 units the following sequence has to apply:

$$\text{AAAA} \overset{K_N}{\rightleftharpoons} \text{BAAA} \overset{K_W}{\rightleftharpoons} \text{BBAA} \overset{K_W}{\rightleftharpoons} \text{BBBA} \overset{K_W}{\rightleftharpoons} \text{BBBBB}$$

I.e, there is one step of nucleation, described by an equilibrium constant K_N, and three steps of growth of the nucleus K_W. According to ref 34 the equilibrium constant for nucleation is expressed in terms of K_W according to

$$K_N = \sigma K_W \tag{8}$$

σ is a measure of the cooperativity of the transition. For $\sigma < 1$ the growth is much more likely than the nucleation; i.e., a sequence will tend to have all units in the same state. For short sequences the transition depends on the length, while for longer chains the transition only depends on K and σ. The degree of transition Θ is related to the apparent equilibrium constant K_{ap} according to

$$K_{ap} = \Theta/(1 - \Theta) \tag{9}$$

For the temperature where half of the units have changed their state from A to B ($\Theta = 0.5$) it follows that

$$\mathrm{d} \ln K_{ap}/\mathrm{d}T = N_0 \Delta H_u / RT^2 \tag{10}$$

ΔH_u is the transition enthalpy for the elementary growth step, (AAB → ABB), and N_0 is the cooperative length

$$N_0 = \sigma^{-1/2} \tag{11}$$

For infinitely long chains ($N \rightarrow \infty$) the average length of A or B sequences at $\Theta = 0.5$ is $N_0 + 1$. More complex models take account of the finite length of chains as well as of the effect of end groups.[36] For the helix–coil transition of pure poly(α-amino acids) typical values of σ are in the range of 10^{-5}.[37]

Adoption of this formalism to the present system requires several assumptions and simplifications. As has been already discussed, the key step is the breaking of the dipole–dipole interaction between the association chains. For two association chains we may describe the melting according to Scheme I. If more than two association chains form an ordered domain, the description of the melting process in Scheme II would apply. A and B correspond to functional groups in the ordered (A) or disordered (B) state. As in the Bragg–Zimm model we will assume infinitely long chains and neglect the influence of chain ends. In addition we assume that the parameters are independent of the number of chains in a domain.

Scheme I

$$\begin{array}{ccccc}
\text{ordered} & & \Theta = 0.5 & & \text{disordered} \\
\text{AAAAAAAAAAA} & \rightarrow & \text{AAAAAA}^{\text{BBBBBB}} & \rightarrow & \text{BBBBBBBBBBBB} \\
\text{AAAAAAAAAAA} & & \text{AAAAAA}_{\text{BBBBBB}} & & \text{BBBBBBBBBBBB}
\end{array}$$

Scheme II

$$\begin{array}{ccccc}
\text{AAAAAAAAAAAA} & & \text{AAAAAAAAAAAA} & & \text{AAAAAAAAAAAA} \\
\text{AAAAAAAAAAAA} & \rightarrow & \text{AAAAAAAAAAAA} & \rightarrow & \text{AAAAAAAAAAAA} \\
\text{AAAAAAAAAAAA} & & \text{AAAAAAAAAAAA} & & \text{AAAAAAAAAAAA} \\
\text{AAAAAAAAAAAA} & & \text{AAAAAA}_{\text{BBBBBB}} & & \text{BBBBBBBBBBBB}
\end{array}$$

Table III
Analysis of the "Melting" According to the One-Dimensional Ising Model[a]

sample	c_{umax}, J/mol·K	$\sigma \times 10^3$	N_0
PB-10-U4A-0.5	636	9.6	10.2
PB-10-U4A-1	747	6.5	12.4
PB-10-U4A-2	1142	2.6	19.8
PB-10-U4A-3	1005	3.1	17.9
PB-10-U4A-4	1037	2.9	18.5
PB-10-U4A-4.5	932	3.6	16.7
PB-10-U4A-7.5	843	4.3	15.3
PB-10-U4A-10	450	14.8	8.2
PB-10-U4A-15	170	124	2.8
PB-10-U4A-20	306	34.5	5.4

[a] σ = cooperativity parameter. N_0 = cooperative length.

According to Ackermann,[37] σ can be derived from the transition enthalpy according to

$$c_{umax} = (4\sigma^{1/2})^{-1} \Delta H_u^{\,2}/(RT)^2 = \Delta c M/(hm) \tag{12}$$

c_{umax} is the maximum value of the excess heat capacity associated with the transition (in J mol^{-1} K^{-1}), ΔH_u is the transition enthalpy with respect to 1 mol of the repeating units within the ordered structure, and T is the temperature of the maximum of the transition curve.

Though the calorimetric experiments were not performed in the limit of heating rate zero, i.e., thermodynamic equilibrium, we attempt to describe the order–disorder transition observed via DSC curves according to the one-dimensional Ising model.

c_{umax} is calculated from the experimental heat capacity change at the peak maximum Δc (in units of mW), the molecular weight of the repeating unit, the sample mass m (mg), and the heating rate h [K/s]. The value of ΔH_u has been chosen from the squalene model compound, assuming that all functional groups are incorporated in the ordered structure in this model compound.

The data obtained according to this analysis from the PB-10-U4A-x series, i.e., c_{umax}, cooperativity parameter σ, and cooperative length N_0, are given in Table III. For the samples PB-10-U4A-2, PB-10-U4A-3, and PB-10-U4A-4, the corresponding cooperativity parameter σ is about 3×10^{-3}. The data show that N_0 passes through a maximum at a value of about 18 for intermediate degrees of substitution (2–5 mol %). For lower and higher functionalizations a smaller value is calculated.

According to this analysis a maximum of about 18 units would be involved in the elementary process of cooperative melting. In the present model this is not the number of functional groups within a domain but the number of contacts between two parallel association chains (Scheme

II). The good agreement between the estimate of the length of the association chain from the present analysis and the approach based on imbalanced stoichiometry[16] is rather surprising. However, it gives some confidence that the description of the observed "melting" endotherm as an order–disorder is reasonable. In the following section a more detailed picture of the structure will be obtained from the SAXS data.

Considerable lower values for N_0 are calculated for the very low degrees of substitution as well as for higher degrees of substitution (>7 mol %). There are some obvious explanations for these findings: at low degrees of substitution the probability of forming long association chains is low; for high degrees of substitution the constraints acting on each functional group suppress the formation of longer association chains. For samples with higher degrees of substitution not only is the fraction of functional groups involved in the ordered domain smaller but also the length of an association chain is strongly reduced.

SAXS. First SAXS experiments on high molecular weight CB10 modified with 4-(3,5-dioxo-1,2,4-triazolin-4-yl)benzoic acid showed a scattering maximum at low angles.[13] As mentioned in the Introduction, this already indicated some kind of a microphase separation between the polar domains and the polybutadiene, in analogy to ionomers.[27–29] In addition, the small-angle scattering pattern became strongly anisotropic upon deformation. The scattering pattern of the deformed sample has been interpreted by a strong orientation of anisotropic scattering centers under uniaxial deformation parallel to the stretching direction and represented the first experimental evidence that the domains formed by the urazole group are not spherical but highly anistropic,[13] a result which has been confirmed by IR dichroism experiments.[17–19]

Another important question not answered in our preliminary work[13] is related to the temperature dependence of the scattering. Especially the question that remained open was whether the SAXS pattern changes upon heating to temperatures above the "order–disorder" transition. In analogy to the problems involved in the SAXS scattering of ionomers it also was not clear whether the scattering results from intraparticle scattering within a domain or is dominated by interparticle scattering. The experiments reported in this section should provide further information to clarify some of these questions concerning the balance between the ordered structure formed by the polar groups and the polybutadiene matrix.

The influence of the degree of modification will be discussed first using a series of modified high molecular weight polybutadienes (CB10-U4A-*x*). These systems showed rather small transitions in their DSC heating traces (see Figure 6) but were easier to handle than samples resulting from low molecular weight polybutadiene. In the second part of this study the temperature dependence of the small-angle scattering will be discussed.

The desmeared scattering patterns of four different samples are shown in Figure 8 as a function of the scattering vector *q*. In all samples a broad scattering maximum is observed. The scattering intensity shows a strong upturn at small angles. Such a behavior is also observed in many other microheterogeneous systems like in ionomers, and no final assignment has been given so far. This upturn of the small-angle X-ray scattering will not be discussed in the following. However, it is our feeling that a complete description of the structure also has to account for this behavior.

The maximum of the rather broad scattering peak shifts to larger values of *q* with increasing degree of polar substitution. According to Bragg's equation this corresponds to a decreasing "periodicity". As seen in Figure 9, the Bragg spacings, calculated from the *q* values of the maximum of the scattering, decrease from 92 Å for CB10-U4A-1 to 48 Å for CB10-U4A-10 (see Table IV).

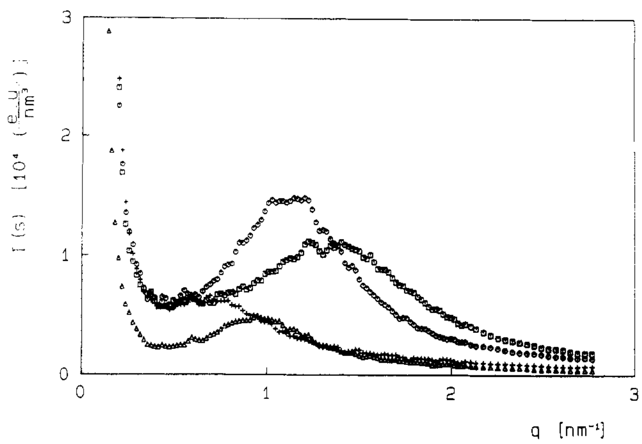

Figure 8. SAXS patterns of CB10-U4A-*x* at 30 °C: (x = 1 mol % (+), 2 mol % (△), 4 mol % (○), 10 mol % (□).

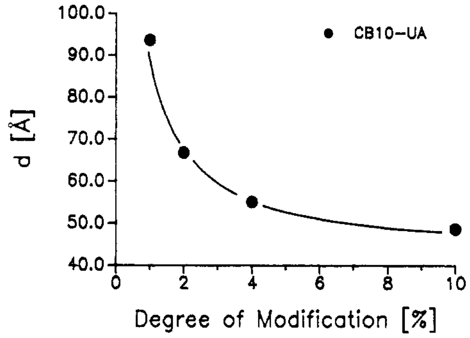

Figure 9. Bragg spacing *d*, calculated from the maximum of the scattering curves as function of the degree of modification of CB10 samples at 30 °C.

Table IV
Analysis of the SAXS Behavior[a]

sample	Bragg distance, nm	vol of primitive cubic lattice, $\times 10^{-19}$ cm^3	N/V	N/D	O_s, m^2/cm^3
CB10-U4A-1	9.4	8.3	88	n.d	n.d
CB10-U4A-2	6.7	3.0	62	n.d	n.d
CB10-U4A-4	5.5	1.6	64	12	72
CB10-U4A-10	4.8	1.1	87	34	408
PB-10-U4A-4	6.3	2.5	96	82	308

[a] N/V = number of urazole groups in a volume element of the primitive cubic lattice. N/D = number of urazole groups incorporated in one ordered domain $N/D = N/V^* f_{\mathrm{ura}}$. O_s = specific inner surface. This value could only be estimated for those samples where the fraction of urazole groups in ordered clusters (f_{ura}) could be determined.

Many SAXS investigations of ionomers were dedicated to the question of whether the ionomer peak is caused by inter- or intraparticular scattering. In the present system, where structure formation is due to directed interactions, the shift of the scattering maximum to larger angles with increasing concentration of functional groups may be taken as an indication that the maximum results from constructive interparticle interference.

If this is correct, the scattering maximum results from the scattering between the aggregates of polar groups and the characteristic distance estimated from the maximum could be related to the distance between center of masses of the domains. The decrease of the Bragg distance with increasing degree of substitution thus would be related to

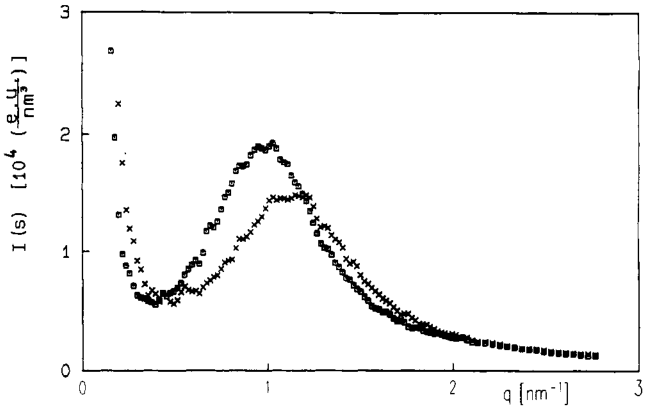

Figure 10. SAXS patterns of PB-10-U4A-4 (□) and CB10-U4A-4 (×) at 30 °C.

an increasing number of scattering centers. The experiments discussed so far can also be explained on the basis of a model based on intraparticle scattering.[30a] Experiments on swollen samples where the structure is not disrupted by the solvent are planned to clarify this question.[30b]

The scattering intensity and the widths of the scattering peaks depend on the concentration of functional groups. For CB10-U4A-4 the scattering maximum is most pronounced. For CB10-U4A-10 the maximum is shifted to larger scattering angles, lower in intensity and considerably broadened. This broadening of the scattering maximum could reflect a rather broad distribution of domain distances and/or domain sizes in the case of the higher substituted sample.

Influence of the Molecular Weight. The influence of the molecular weight of the polybutadiene backbone on the quality of the ordered structure, which already became evident in the DSC experiments (Figure 6), is also reflected in the scattering behavior. The desmeared scattering curves of PB-10-U4A-4 and CB10-U4A-4 are shown in Figure 10. The scattering peak of PB-10-U4A-4 is much narrower and more intense compared to the scattering maximum of the sample derived from the high molecular weight polybutadiene. In addition, the position of the peak maximum is shifted to smaller *q* values in the case of the PB-10 sample, indicating a larger distance between the scattering centers. This is in agreement with the DSC results. The smaller scattering intensity of the higher molecular weight sample is the result of an increased fraction of functional groups which are not incorporated in ordered domains. As a consequence the electron density difference $\Delta\rho$ between the ordered domains and the surrounding matrix is considerably smaller in CB10-U4A-4 compared to PB-10-U4A-4. It must be emphasized again that the scattering contrast mainly results from the density difference between the polybutadiene matrix—in which a rather large portion of the polar groups may be dispersed—and the supramolecular ordered junction zones.[38]

From the Bragg distance the number of functional groups which are incorporated in an ordered domain can be estimated (assuming interparticle scattering). For this purpose the domains are put onto a primitive cubic lattice with length *d*. From the concentration of groups the number of urazole groups in such a hypothetical unit cell N/V can be calculated. The data are also given in Table IV. The overall number of polar groups per primitive cubic unit cell N/V is between 60 and 100.

Thus the actual number of functional groups in the supramolecular orderd domain may vary between 20 and 90. For PB-10-U4A-4 a value of 86 is calculated. If 18 units form the association chain (see above), about 5 association chains aggregate to an ordered domain. For the high molecular weight polybutadienes, the DSC maximum is much less pronounced (see Figure 6). For CB10-U4A-4 N_0, the cooperative length, is only about 5–8. Taking the value of $N/V = 64$ and the reduced fraction of groups in the ordered domains, the average number of association chains forming a domain is 2–4. For these two samples which have the same concentration of functional groups this rough estimation shows that, compared to CB10-U4A-4, PB-10-U4A-4 forms larger but fewer, more perfectly organized domains, a result which already has been derived qualitatively from Figure 10.

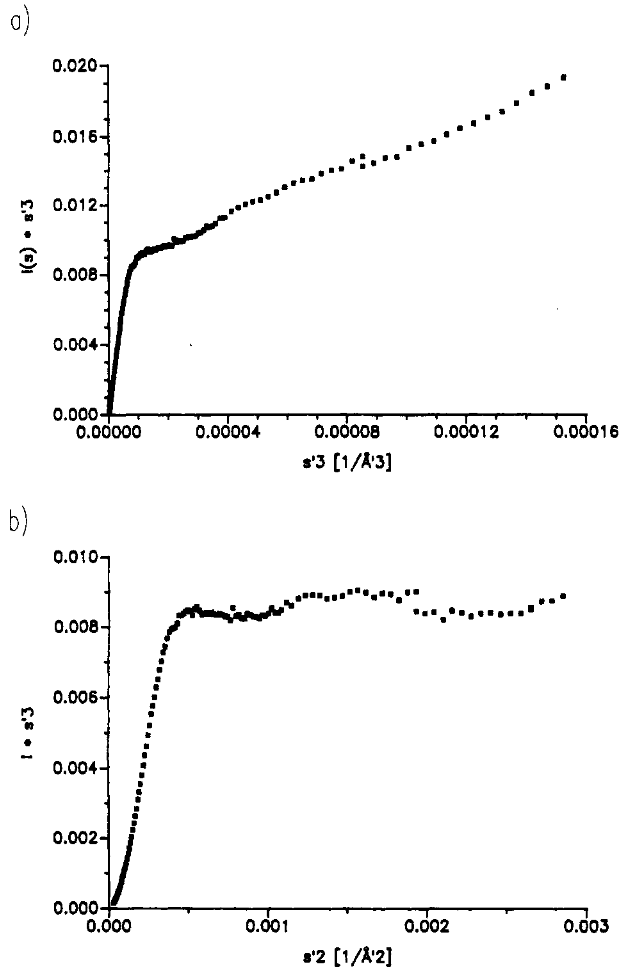

Figure 11. (a) Analysis of the SAXS data according to the Porod law. Plot of (I(**s**) **s**^{3} versus **s**^{3} for sample CB10-U4A-10 for the determination of the background scattering and K_p. (b) Analysis of the terminal zone of the SAXS curve according to Ruland.[26] Plot of I***s**^{3} versus **s**^{2}.

Increasing the concentration of functional groups in the high molecular weight polybutadiene increases the number of domains, but the size and perfection of these domains decreases.

Parts a and b of Figure 11 show typical plots of the slit-smeared scattering data according to the Porod analysis. From graphs like those in Figure 11a, the background scattering and the Porod constant K_p are obtained. According to Ruland the thickness of the phase boundary *E* may be estimated from a plot of I***s**^{3} versus **s**. All samples gave very similar plots, and due to the small slope the error in the determination of *E* is rather large. A value around 2 Å is determined from the Porod analysis independent of the sample.

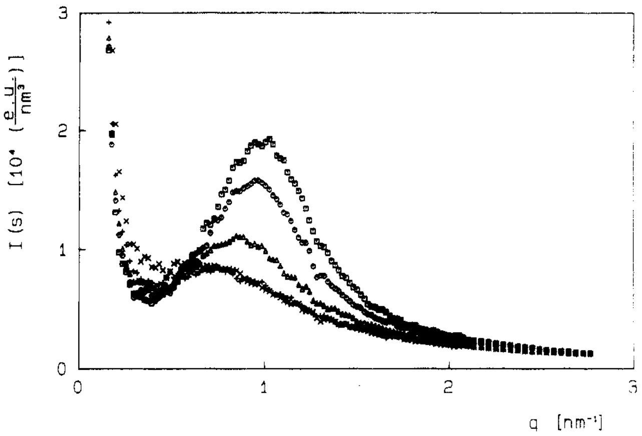

Figure 12. Small-angle X-ray scattering of sample PB-10-U4A-4 at various temperatures: 30 °C (□), 70 °C (○), 80 °C (△), 95 °C (+), 120 °C (×).

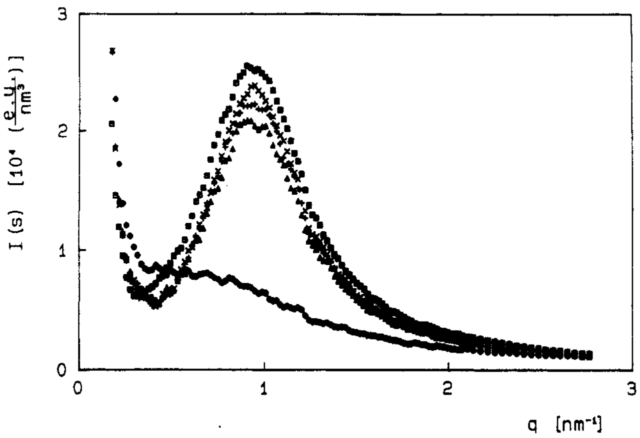

Figure 13. Time dependence of the scattering peak of modified PB-10-U4A-4 after heating up to 120 °C; (□) room temperature, before heating; (○) 120 °C; (△) room temperature, 30 min after cooling; (+) room temperature, 1 h after cooling; (×) room temperature, 5 h after cooling.

As has been outlined in the Experimental Section, another important quantity which characterizes phase-separated systems is the specific inner surface O_s. First the invariants Q are obtained according to eq 6. Extrapolation to large scattering vectors is necessary for evaluating eq 6 and may cause considerable errors in the value of Q. In addition the volume fractions of the two phases are not exactly known, because a considerable part of the polar groups is not involved in structure formation.

Nevertheless, the data of the samples CB10-U4A-4 and CB10-U4A-10 for O_s, which were calculated using the fraction of effectively contributing urazole groups f_{ura} to estimate the volume fractions of the two phases, show that the internal surface strongly increases with increasing degree of substitution. In connection with the decreasing size of the elementary cell this means that the number of domains increases, while the size is affected only by a factor of 3. Comparison of the specific inner surfaces of the high and low molecular weight systems, both containing 4 mol % of functional groups, shows that the size of the domain increases by a factor of 7–8.

Temperature Dependence of the Small-Angle X-ray Scattering. A direct correlation of the observed DSC behavior and the small-angle X-ray scattering would give further support for the structural picture given in Figure 2.[13-16]

The SAXS patterns obtained for various temperatures for sample PB-10-U4A-4 are shown in Figure 12. While the scattering maximum is little affected at temperatures $T < 60$ °C, the maximum disappears in the temperature range between 70 and 95 °C, i.e., in the same temperature regime where the DSC endotherm is observed. This is observed for all other samples (CB10-U4A-*x* series).

The temperature range over which the scattering maximum disappears covers 25 °C. At each temperature the sample was kept for 30 min (exposure time) after reaching thermal equilibrium. The position of the scattering maximum shifts to smaller scattering values with increasing temperature. Thus the observed decrease of the scattering intensity most obviously is related to the subsequent melting of ordered domains of different size, the smaller ones melting at lower temperatures. As a consequence, the average distance between scattering centers increases.

Another important question with respect to the organization of self-organizing polymer systems is related to the kinetics of structure formation. First, it is important to check reversibility in the system; second, the dynamics may be of importance regarding the processing and mechanical properties of such materials. As already mentioned above, the kinetics of structure formation can be followed by IR spectroscopy.[22,24] The observation of the re-formation of the maximum in small-angle X-ray scattering after quenching from high temperatures is another possibility. However, time resolution of this experiment is rather limited, if only a rotating anode is available as the X-ray source as has been in the present experiments. Figure 13 shows the scattering patterns of PB-10-U4A-4 recorded at 30 °C at different times after heating the sample to 120 °C. After about 5 h, the scattering is very close to the original pattern. During this annealing time the position of the scattering maximum does not change. However, an improved time resolution would be necessary to decide whether structure formation can be described by a homogeneous nucleation.

According to the qualitative arguments developed above for the melting behavior, a constant position of the scattering maximum would arise from a constant number of growing scattering centers which would form in the very early beginning of the process. Thus the growth of the ordered domains could be described by a diffusion-controlled process of functional groups to such nuclei. This, however, is still speculative and needs further experimental evaluation.[24]

Finally another interesting feature observed in the temperature-dependent scattering data will be discussed. It is observed in all samples but is more pronounced in the samples based on the high molecular weight polybutadienes, especially at the higher degrees of substitution. Typical sets of data are shown in Figure 14a,b for CB10-U4A-4 and CB10-U4A-10. At room temperature the scattering maximum related to the interparticle distance of the ordered domains is observed at $q = 1.1$ and 1.35 nm^{-1}, as well as the upturn at low q values. Upon raising the temperature the maximum disappears at about 70 °C, which corresponds to the DSC "melting" transition for these samples. At higher temperatures at new scattering maximum at even lower q values shows up. Up to 120 °C, which was the highest temperature we did the SAXS experiments; before irreversible cross-linking of the polybutadiene started to interfere, this new maximum increases in intensity. As a characteristic feature it always is lower in intensity as the scattering maximum which results from the spacing of the ordered domains, and its intensity is larger for larger primary chains and higher degrees of substitution.

A possible, though still speculative, explanation is that this scattering maximum observed at high temperatures

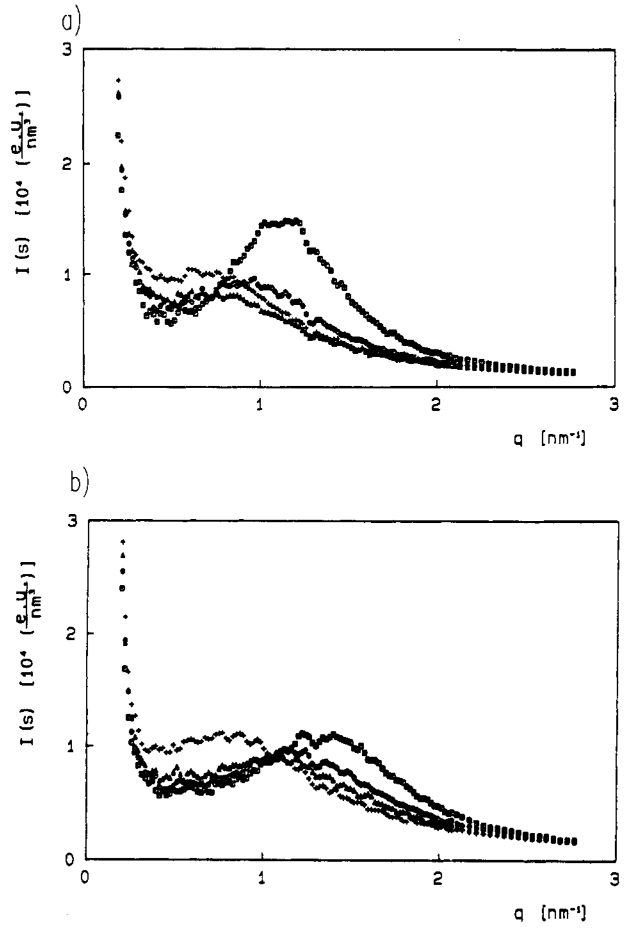

Figure 14. (a) Small-angle X-ray scattering curves of sample CB10-U4A-4 at various temperatures (30 °C; (□; 70 °C; ○, 80 °C; △; 95 °C; +). (b) Small-angle X-ray scattering curves of sample CB10-U4A-10 at various temperatures (30 °C; □; 70 °C; ○; 80 °C; △; 95 °C; +).

results from a demixing between the unpolar polymer matrix and the association polymers, which are still present at these temperatures. The resulting "phase-separated" structure would show a considerable lower electron density difference between the polybutadiene-rich and polybutadiene-poor phases, and the functional groups would show a high mobility.

A similar behavior was observed by Russell et al. in the case of a supramolecular structure forming ionomer system.[39]

IV. Discussion

The experimental findings from both DSC and SAXS experiments are in agreement with our model of the supramolecular structure formed by the functional groups attached statistically along the polybutadiene backbone (Figure 2). The variation of the SAXS maximum with temperature supports our previous interpretation that both DSC and SAXS probe the same supramolecular ordered structure.[14] Both methods are very sensitive to characterize the order–disorder transition in this unique system.[40] The change in the scattering behavior occurs at the same temperatures where the DSC endotherm and the transition from rubbery to flow behavior[15] was observed.

Especially the SAXS investigations show that the multiphase structure of the system is due to the supramolecular ordered zones, i.e., that microphase separation is not just caused by simple demixing due to the different polarity of association chain polymer and polybutadiene. The additional scattering maximum at lower angles observed at temperatures above the order–disorder transition may be the result of a "simple" microphase separation as has been discussed above. Similar chemical systems, e.g., polybutadienes modified with 4-phenyl-1,2,4-triazoline-3,5-dione, do not show a SAXS peak.[41] On the other hand, the typical scattering peak of ionomers is not reversibly temperature dependent.

The portion of ordered groups is strongly influenced by the degree of modification i.e., the number of functional groups per "unit length of polymer chain" present. Thus an interesting case is realized here: at low concentrations the behavior is dominated by the self-assembling of the functional groups, while at higher concentrations the supramolecular structure hinders further self-assembling. Such a behavior might also be called anticooperative, while the structure formation itself is a cooperative process. Formation of the ordered domains alters the mobility and accessability of functional groups which are not yet incorporated into the supramolecular structure; i.e., structure formation causes an internal quench. This topological hindrance depends on the concentration of groups as well as on the number of groups per chain, if the constraints have a long lifetime as is the case for the present system.

Structural perfection, i.e., the size of the ordered domains, depends on the molecular weight of the base polymer. For the lower molecular weight system the transition temperature is slightly higher, as well as the transition enthalpy. This also results in a sharper SAXS peak.

Polymer backbones of different chemical nature may behave differently with respect to supramolecular structure formation.[42] Those groups which are not incorporated in the structure are nevertheless likely to be complexed in hydrogen-bonded dimers or multimers.

The supramolecular structure formed by the 4-urazoylbenzoic acid groups in the polymer melt is very specific and strongly depends on the exact local chemical structure. This has been confirmed by experiments where the urazole heterocycle is fixed at the media position of the benzoic acid.[21] Though the same functional groups are present the experimental data give no indication for a supramolecular ordering of the functional groups: These samples did not show an endothermic transition in the DSC and no temperature-dependent SAXS peak.[22] In addition, the mechanical properties are very similar to the systems where only binary hydrogen bonds are formed. As has been mentioned in the Introduction, strong dipole–dipole interactions between urazole units were identified as the molecular driving force of the unusual supramolecular self-assembling process in these modified polydienes.

The resulting two-dimensional array, as indicated in Figure 1, is highly anisotropic. In the case of the modified polybutadiene, the polymer segments are linked to this highly ordered structure from the top and from the bottom, as are the butenyl moieties in the case of the low molar mass model compound.[6]

Our present understanding concerning the limitations and opportunities for supramolecular structure formation of statistical copolymers is still too limited to give a final picture of which types of material properties may be achieved. Besides a deeper understanding of the system presented in this paper more synthetic work is necessary to evaluate this interesting class of self-assembling materials. Future work will also have to consider the properties of these materials in solution as well as materials where the polar groups are not attached statistically along the polymer backbone.

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