Multiphase thermoplastic elastomers by combination of covalent and association chain structures: 2. Small-strain dynamic mechanical properties[*]

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Polybutadienes of narrow molecular-weight distribution, carrying statistically distributed polar phenylurazole (**1**), 4-ethoxycarbonylphenylurazole (**2**) and 4-carboxyphenylurazole (**3**) groups along the polymer chain, are analysed with respect to their dynamic mechanical properties in the linear viscoelastic region. In these systems thermoreversible networks are formed by hydrogen-bond complexes. In the case of **1** and **2**, where only binary complexes are formed, the systems show thermorheologically simple behaviour, i.e. the construction of viscoelastic master curves is possible and the temperature dependence is described by an average apparent activation energy of flow for all relaxation processes. For polybutadiene carrying between 0.5 and 4 groups of **3** per 100 repeat units, thermorheologically complex behaviour is observed, which is related to the multiphase structure formed by phase separation between the covalent polybutadiene backbone and supramolecular ordered association polymers formed by the polar functional groups.

(Keywords: thermoplastic elastomers; association polymers; cooperative structure formation; hydrogen bonds; dynamic mechanical analysis)

INTRODUCTION

During the last two decades thermoplastic elastomers (TPEs) based on block copolymers have been of great interest due to their steadily increasing commercial importance[1].

Unique property combinations of rubber elasticity at application temperature and melt processability have been realized for a large variety of chemical structures like styrene–butadiene–styrene (SBS) triblock copolymers or multiblock copolymers composed of polyether soft segments linked to polyamide, polyester or polyurethane hard segments. Phase separation either by crystallization of the hard segment or by immiscibility of the amorphous polymer components plays a dominant role in structure formation. The final properties result from a delicate balance of microstructure, composition, block molecular weights and processing.

Block copolymer synthesis requires highly specialized polymerization techniques. As a consequence, many technically interesting elastomers are not available as TPEs.

One alternative to block copolymers is the introduction of ionic groups, where the linkages are formed by ionic multiplets and clusters[2]. However, polymer analogous reactions often require reaction conditions that result in uncontrolled branching and crosslinking. In addition, processing of ionomers requires the use of processing aids like metal stearates, which plasticize the ionic domains. Another approach using ionic interactions involves blends of acid- and base-terminated telechelic polymers that have a microstructure similar to that of multiblock copolymers[3].

We have recently developed a new strategy for the preparation of multiphase polymer systems, which allows preparation of TPEs from all kinds of polydienes[4,5]. The concept, based on the combination of covalently linked monomer units (polydiene) with a polymer formed by reversible association, is shown schematically in *Figure 1*.

Starting from the polydiene, difunctional units

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are introduced statistically by a polymer analogous reaction. The functional groups are able to form strong binary hydrogen-bond complexes. As a consequence a second macromolecular structure is formed by multistep association. Phase separation, resulting from cooperative supramolecular ordering, stabilizes the reversible network. The details of the chemical structure of the polar units play a dominant role in supramolecular structure formation[6]. The structural unit for which the formation of a multiphase structure is observed is the 4-(4′-carboxyphenyl)urazole (UA) group. Details on the synthesis of

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[*] Dedicated to Professor Walther Burchard, whose contributions broadened our view of thermoreversible networks, on the occasion of his 60th birthday

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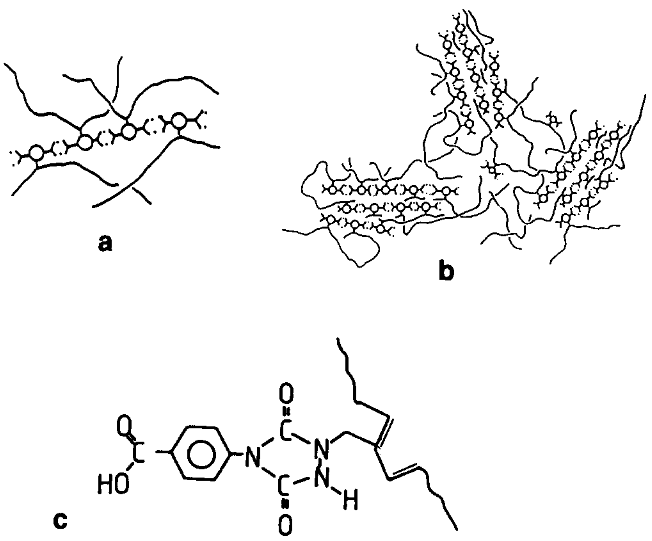

Figure 1 Schematic structural model for the build-up of a multiphase structure from statistical copolymers: (a) formation of the association polymer; (b) phase separation by cooperative aggregation; and (c) resulting structure from the addition of 4-(4′-carboxyphenyl)-1,2,4-triazoline-3,5-dione to a polybutadiene chain. The -COOH and the -NHCO- units are able to form hydrogen-bond complexes

the materials are reported elsewhere, in part 1 of this series[5].

The existence of a phase-separated structure in agreement with the scheme shown in *Figure 1* has been proved by SAXS and d.s.c.[4,5]. The supramolecular ordering gives rise to a melting endotherm and a scattering maximum at low angles ($2\theta = 4°$). The stress–strain behaviour of this new type of multiphase material resembles that of multiblock copolymers with distinct yielding, strain softening and high tensile strength.

In the present paper a more detailed study of the dynamic mechanical properties at small strains will be given and the properties will be compared to corresponding systems where the acid is esterified or where no additional functional group at the phenyl group is present. In the latter system, which has been studied in great detail, only binary hydrogen-bond complexes are formed[7–11].

Both temperature and frequency dependence will be discussed and it will be shown that the mechanical data support the picture of a phase-separated structure formed by the combination of covalent and association chain structures.

EXPERIMENTAL

Polybutadienes were prepared by anionic polymerization in cyclohexane as solvent. The urazole groups are introduced by the fast and quantitative polymer analogous reaction of the corresponding 1,2,4-triazoline-3,5-diones with the polybutadiene in tetrahydrofuran (THF) solution[7,12,13].

The synthesis of the ester and the acid-substituted triazolinediones is reported elsewhere, in part 1 of this series[5].

The designation of the materials used throughout this study describes the polymer, polybutadiene (PB), its molecular weight (in 1000), the moiety attached by the polymer analogous reaction (PU for phenylurazole, UA for phenylurazole acid, UE for phenylurazole ester), and the degree of modification (mol%) with respect to the repeat unit of the polybutadiene.

Viscoelastic measurements

Viscoelastic measurements were performed in an Instron 3250 rheogoniometer in oscillatory mode. The parallel-plate geometry was used throughout these studies, with the exception of the PB-26-PU samples, where cone–plate geometry was used. Amplitudes were kept in the linear viscoelastic region. The frequencies ranged from 0.0443 to 7.5 Hz. Measurements were performed at different temperatures. For systems with binary hydrogen-bond complexes, the temperature range covered 220–330 K, while the PB-30-UA-4 sample was measured up to 360 K. Usually measurements were performed every 10 K.

Special care was taken with regard to the temperature dependence of the measurement geometry of the rheometer system. Data were directly converted into ASCII code. All computations were performed on a HP9825 desk-top computer.

RESULTS

The mechanical properties of polybutadiene carrying various amounts of PU groups have been studied in detail[7–11]. In this system it is possible to obtain viscoelastic master curves by horizontal shifting of the isotherms.

The time–temperature superposition principle holds in this system though the hydrogen bonds make an additional contribution to the apparent activation energy of flow[10]. The material can be characterized as thermo-rheologically simple[12]. In comparison with the corresponding unmodified polybutadiene, the rubbery plateau is broadened to lower frequencies but only slightly increased. No equilibrium modulus contributes to the mechanical relaxation.

The same behaviour is observed for polybutadienes carrying the phenylurazole ester groups. This is shown in *Figures 2* and *3*, where the storage and loss modulus master curves are shown as a function of reduced frequency at a reference temperature of 273 K for the parent polybutadiene (PB-30-0) and two samples carrying 2 and 4 mol% of the ester (PB-30-UE-2, PB-30-UE-4).

As for the phenylurazole substituent, the transition from rubbery plateau to flow is shifted to lower frequencies and becomes broader due to a broadening of the relaxation time spectrum.

It has to be concluded that the ester group does not interfere with the binary hydrogen-bond complexes formed between the urazole groups.

In *Figure 4* the set of isothermal storage modulus data of sample PB-30-UA-0.5 is plotted as a function of frequency. Already for such a low degree of substitution (0.5 mol% corresponds to an average of 2.8 groups per chain), no composite master curve can be formed by horizontal shifting of the isothermal data. Moreover, the frequency-dependent isotherms can be divided into three categories. At low temperatures the modulus remains nearly constant over the whole frequency range. The modulus frequency curves are linear ($d \log G'/d \log \omega \sim 0.2$) in the temperature range from 220 to 290 K. Within a temperature range of about 20 K the behaviour switches to a strong frequency dependence. However, the curves

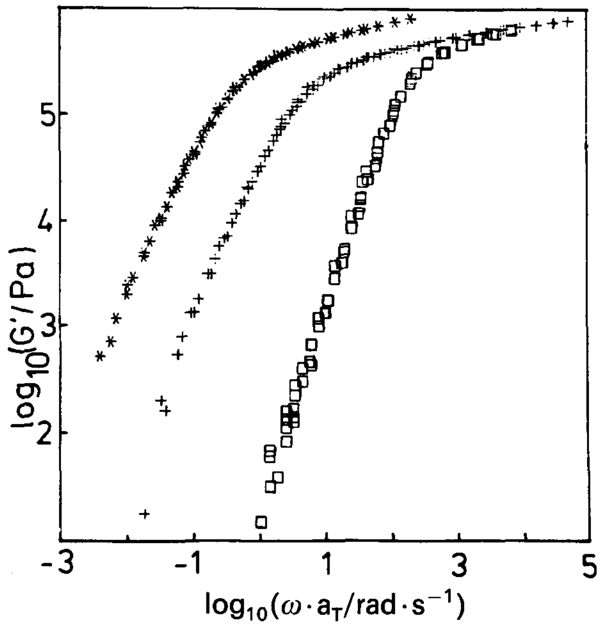

Figure 2 Storage modulus master curves for PB-30-0 (□), PB-30-UE-2 (+) and PB-30-UE-4 (∗); reference temperature 273 K

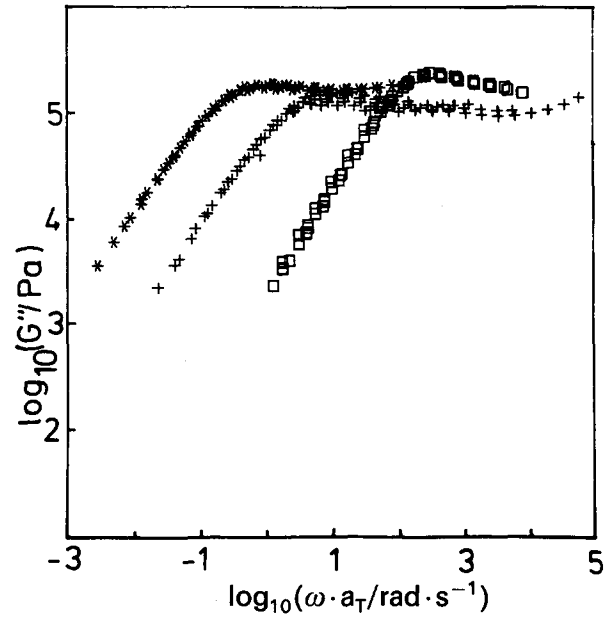

Figure 3 Loss modulus master curves for PB-30-0 (□), PB-30-UE-2 (+) and PB-30-UE-4 (∗); reference temperature 273 K

obtained for different temperatures are still rather linear. At the highest temperatures the expected behaviour of $d\log G'/d\log\omega \sim 1.8$–$2.0$ is observed.

The same features as for PB-30-UA-0.5 are observed for the samples with higher degrees of polar substitution (1, 2 and 4 mol%), but the transition zone, which separates the temperature region of small and strong frequency dependence of the modulus, is shifted to higher temperature.

The three different regions can also be distinguished by comparing the behaviour of $G'(\omega)$ and $G''(\omega)$. This is shown in *Figure 5* where $G'(\omega)$ and $G''(\omega)$ are plotted for three temperatures. At the lowest temperature G' is larger than G'' in the whole frequency range, characteristic for the rubbery plateau. G' shows the slight frequency dependence discussed above; G'' is nearly constant with frequency, showing only a very weak maximum at about 1 rad s^{-1}. At the highest temperature G'' is larger than G' and approaches the expected $G'' \propto \omega$ dependence, which is characteristic for polymeric liquids. In the intermediate region at 302 K a situation is realized where G' equals G'' in the whole frequency region under investigation. The slope is 0.5 in that case.

A similar power law has been reported for gelling systems close to the gel point[14–17], for block copolymers close to the order–disorder transition[18], and also for phase-separated polymer blends, where phase separation can be expected to occur according to spinodal decomposition[19].

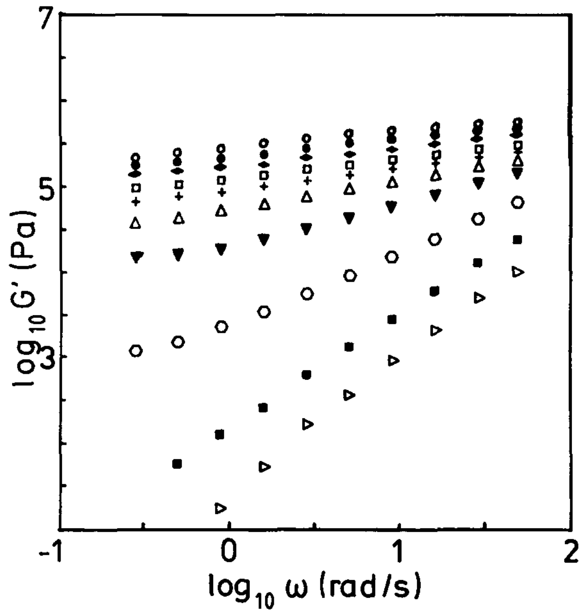

Figure 4 Set of isothermal storage modulus data for PB-30-UA-0.5 sample. Temperatures: (○) 231 K; (●) 243 K; (◆) 253 K; (□) 273 K; (+) 283 K; (△) 293 K; (▼) 302 K; (○) 313 K; (■) 323 K; (▽) 333 K

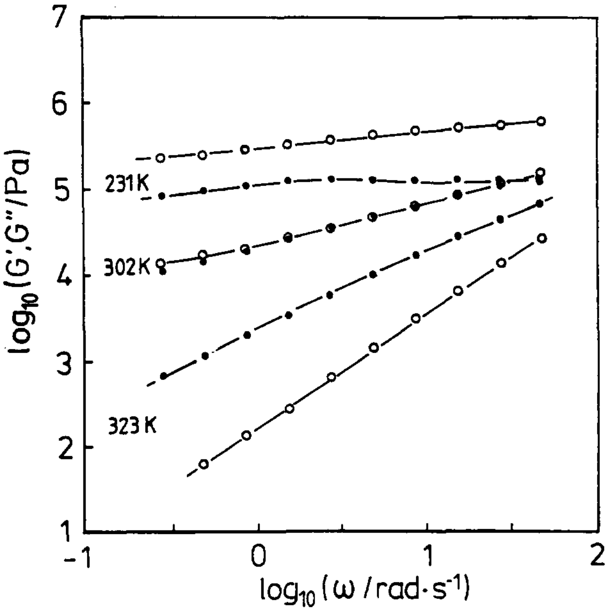

Figure 5 Isotherms of G' (○) and G'' (●) for PB-30-UA-0.5 sample; temperatures as indicated

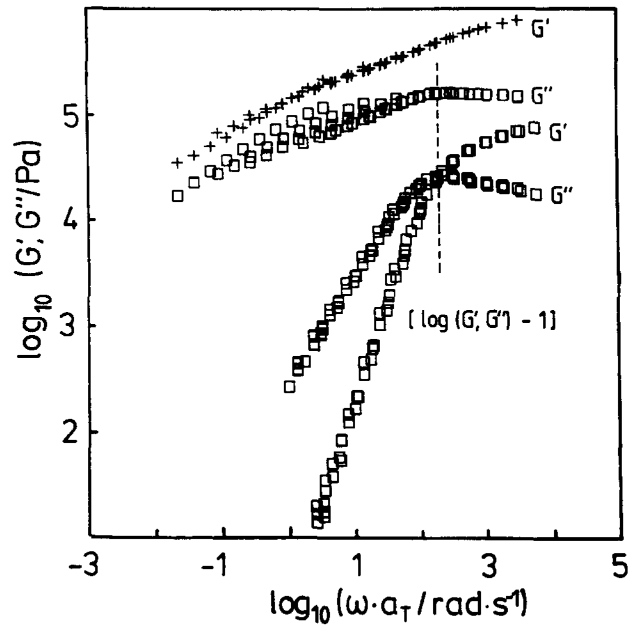

Figure 6 Master curves for G' and G'' (as indicated) for PB-30-0 (lower set of curves) and PB-30-UA-0.5 (upper two curves); for PB-30-UA-0.5 only the lower temperatures were used to obtain the apparent master curve ($T < 300$ K); the curves for PB-30-0.5 are shifted 1 decade along the ordinate to avoid overlap

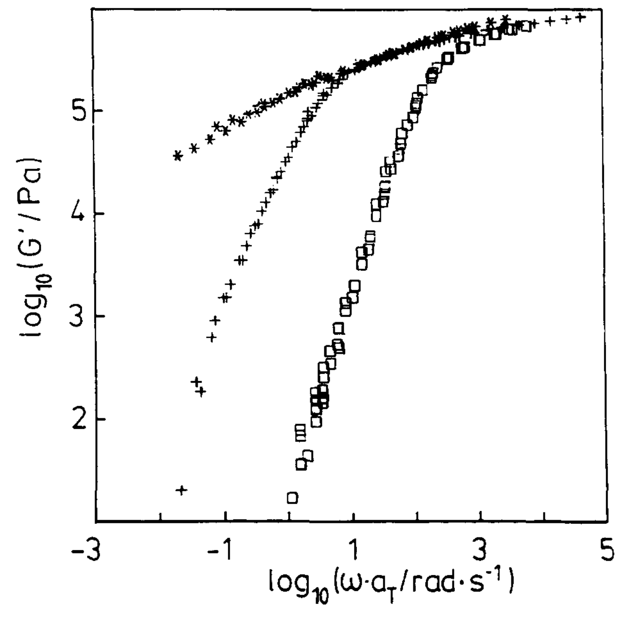

Figure 7 'Apparent' storage modulus master curves for PB-30-0 (□), PB-30-UE-2 (+) and PB-30-UA-0.5 (∗); reference temperature 273 K

In order to compare the behaviour of PB-30-UA-0.5 with the parent PB and the phenylurazole ester-modified PB (PB-30-UE-2), an 'apparent' master curve was obtained from the low-temperature data. As can be seen in *Figure 6* an apparently smooth master curve was obtained from these low-temperature data for G'. However, failure of the time–temperature superposition principle becomes evident if the G'' data are shifted using the same log a_T values. The data are compared to the parent PB, and the large difference in the width of the rubbery plateau region is evident. A weak loss modulus maximum is observed at the same reduced frequency where G'' has its maximum for the PB-30-0.

The additional effect of the acid group is even more striking, when comparing the apparent master curve of PB-30-UA-0.5 with that of PB-30-UE-2 with four times the number of polar groups (*Figure 7*). While in PB-30-UE-2 the rubbery plateau changes smoothly to the terminal flow zone, no such behaviour is observed in PB-30-UA-0.5.

As outlined above, the reduction of the temperature- and frequency-dependent data to a master curve is not possible for the urazole acid system (thermorheologically complex behaviour). The following discussion will thus focus on the temperature dependence of the mechanical properties at a given frequency (0.14 Hz = 0.9 rad s^{-1}).

In *Figure 8* data of polybutadiene PB-26-0 carrying various amounts of phenylurazole groups are shown (PB-26-PB-x). The influence of the binary hydrogen-bond complexes shows up in a decreasing slope of the log G'/T curve with modification. The transition from the rubbery plateau to flow spreads over an extremely broad temperature region. This results from the shift of the complex equilibrium towards more free functional groups with increasing temperature. The same behaviour is observed for polybutadiene carrying urazole ester groups. In *Figure 9* storage moduli of unmodified polybutadiene PB-30-0, urazole ester-modified sample PB-30-UE-2 and the corresponding acid PB-30-UA-2 are plotted as a function of temperature. The tremendous difference when changing from the acid to the ester is evident from this figure. In the experimental temperature range no plateau is seen for PB-30-0 at 0.14 Hz; the transition from rubbery plateau to flow is in the range of 240–280 K for the ester, while a constant (or even slightly increasing) modulus is obtained for PB-30-UA-2 up to a temperature of 330 K. Then the modulus drops steeply within a temperature range of 20 K.

These features are shown in *Figure 10* for a series of different concentrations of polar groups. Already for 0.5 mol% polar units this characteristic behaviour is observed: a constant plateau followed by a narrow transition zone. In this case the transition occurs at about 293 K, increasing to 348 K for the 4% modified sample.

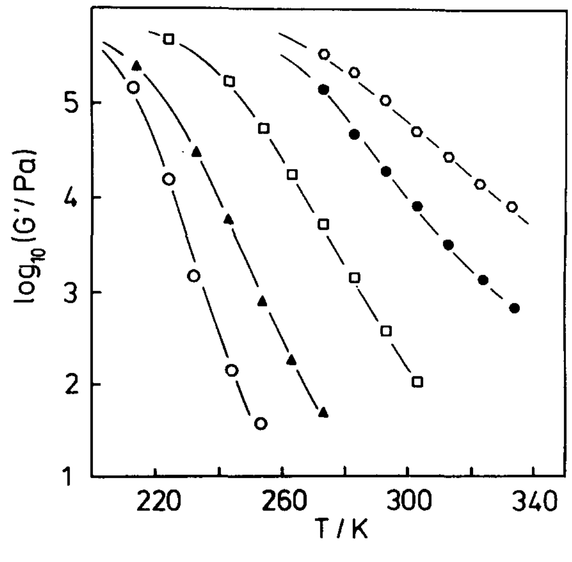

Figure 8 Temperature dependence of the storage modulus G': PB-26-0 (○); PB-26-PU-0.5 (▲); PB-26-PU-2 (□); PB-26-PU-5 (●); PB-26-PU-7.5 (○); frequency 0.14 Hz

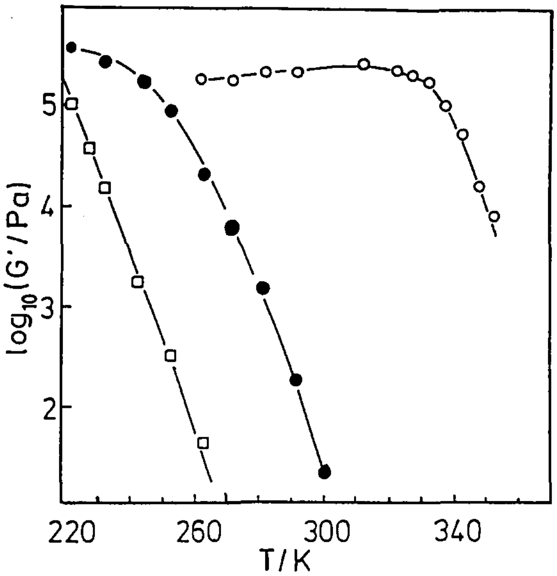

Figure 9 Temperature dependence of the storage modulus G': PB-30-0 (□); PB-30-UE-2 (●); PB-30-UA-2 (○); frequency 0.14 Hz

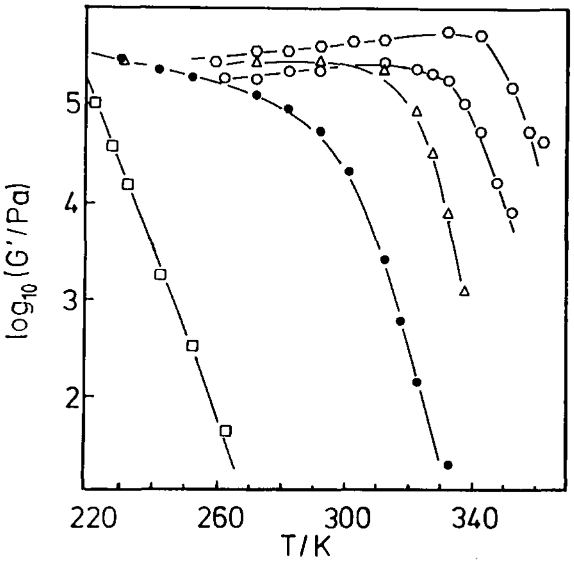

Figure 10 Temperature dependence of the storage modulus G': PB-30-0 (□); PB-30-UA-0.5 (●); PB-30-UA-1 (△); PB-30-UA-2 (○); PB-30-UA-4 (○); frequency 0.14 Hz

Further increase of the number of polar groups increases the modulus in the rubbery plateau zone with almost no shift of the transition to even higher temperatures.

DISCUSSION

The results presented in the previous section give additional information on the structure of these elastomers carrying complex functional groups. The major observations when switching from the ester derivative to the acid are failure of the time–temperature superposition principle, extreme broadening of the rubbery plateau to higher temperatures and low frequencies and a narrow transition zone from the rubbery plateau to flow at high temperatures. The shift of the rubbery plateau to high temperatures makes these materials new candidates for thermoplastic elastomers. The change of the mechanical properties cannot be related to the change of the glass transition temperature, which increases upon introduction of polar groups[12,20]. As has been reported previously[5] the glass transition temperatures of the ester system increase more strongly (about 13 K from PB-30-0 to PB-30-UE-4) than for the acid derivative (about 7 K for PB-30-UA-4). The increase of T_g is related to the decrease in segmental mobility. The smaller increase for the acid system means that the acid does not decrease the local segmental mobility to the same degree as the ester system. Another interesting observation can be made if the mechanical properties are compared to butadiene–methacrylic acid copolymers[21]. In that system T_g increases with modification, and the effect of the carboxylic acid groups on the terminal mechanical behaviour is rather weak. Only upon neutralization of the acid with $LiOCH_3$ to obtain the corresponding ionomer do elastomer-like properties arise, again associated with a further increase of T_g.

The properties of the present system clearly differ from those of ionomers, where for systems with low amount of ionic groups (<5 mol%) thermorheologically simple behaviour has been reported[22,23]. Only for higher concentrations does the system switch to thermorheologically complex behaviour.

According to the condition for the validity of the time–temperature superposition principle[13] and the work of Tschoegl *et al.*[24] on the linear viscoelastic behaviour of multiphase polymers like SBS triblock copolymer, thermorheologically simple behaviour is expected for systems where all relaxation processes occurring in a given system on different length scales should have the same temperature dependence. This implies that the system can be described by a single (or average) friction coefficient. This is not the case if the system undergoes a structural transition in the temperature range of investigation.

In the urazole acid system, the time–temperature superposition clearly fails, even for the lowest degrees of substitution. Moreover the rubber–melt transition occurs in the same temperature region in which an endotherm is observed by d.s.c. This 'melting' is related to the cooperative breakdown of the supramolecular structure formed by the association polymer as shown in *Figure 1b*.

In this first analysis of the dynamic mechanical properties of a new class of multiphase polymeric materials many problems, especially concerning the frequency dependence, remain unanswered. The results so far provide additional support for the structural model presented in *Figure 1b* for the build-up of multiphase materials from statistical copolymers by a cooperative structure formation.

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