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ORIGINAL CONTRIBUTION

B. Schartel
V. Stümpflen
J. Wendling
J.H. Wendorff
W. Heitz
R. Neuhaus

Rigid star-shaped multipodes: molecules designed for molecular reinforcement

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B. Schartel · V. Stümpflen
J. Wendling · J.H. Wendorff (✉)
Fachbereich Physikalische Chemie
und Wissenschaftliches Zentrum
für Materialwissenschaften
Philipps-Universität Marburg
35032 Marburg, FRG

W. Heitz · R. Neuhaus
Fachbereich Physikalische
Chemie–Polymere
Philipps-Universität Marburg
35032 Marburg, FRG

Abstract Star-like rigid multipodes consisting of an adamantane core and rigid oligophenylenes arms with various lengths were synthesized with the aim to induce molecular reinforcement effects in mixtures of such multipodes with polymer matrices. The expectations based on theoretical considerations were that multipodes display an enhanced solubility both in low molar mass solvents and in polymer matrices. We investigated the shape of such multipodes, their structure formation and dynamics in the condensed state as well as their miscibility. The finding is that the peculiar shape of such multipodes does not prevent a dense packing and crystallization in the condensed state. The solubility in low molar mass solvents can be enhanced by up to three orders of magnitude just by increasing the arm length by one phenyl group. Finally, we consider the properties of mixtures of such multipodes with polymer matrices.

Key words Molecular reinforcement – rigid multipodes – miscibility – structure

Introduction

Rigid chain molecules display a strong tendency towards immiscibility with flexible chain molecules, for entropic reasons. This has been clearly demonstrated by Flory based on lattice calculations [1, 2]. These predict that compatibility exists, in general, only for very high concentrations of the solvent. No miscibility is expected for the binary mixture of the two polymer species.

This theoretical result turned out to have a strong impact on activities directed at the development of molecularly reinforced systems. The concept of molecular reinforcement is based on the assumption that the dispersion of linear rigid molecule in a matrix will lead to an increase of the modulus along the direction of orientation of the molecule very similar to the case of macroscopical fibers [3–6]. Computer simulations employing a force field approach have demonstrated that the concept of molecular reinforcement is, in principal, sound [7]. The major obstacle which has to be circumvented in this approach is thus the strong immiscibility of rigid and flexible chain molecules.

Some time ago, we predicted on the basis of lattice calculations that non-linear rigid multipodes composed of rigid linear segments such as cross-like or star-like molecules should display an enhanced solubility both in solvents and polymer matrices and should thus be favorable systems for molecular reinforcement [8–12].

This contribution is concerned with experimental studies and computer simulations on such multipodes. It considers the synthesis, the characterization of the shape of the rigid molecules, the structure of the condensed phase formed by them, their solubility in solvents and polymer matrices and finally optical and dielectric properties.

Experimental

1,3,5,7-Tetrabromo-adamantane

Adamantane (13.5 g, 0.1 mol) was added portionwise to a stirred mixture of anhydrous aluminum chloride (13.5 g, 0.1 mol) and bromine (175 g, 1.1 mol) at 5–10 °C. The mixture was heated to 70 °C and held at that temperature for 24 h. Hydrogen bromide was evolved during the whole reaction. The mixture was then cooled to room temperature and hydrolyzed with 40 ml of diluted hydrochloric acid. The excess of bromine was reduced with aqueous sodium sulfite. After the extraction of the product with 150 ml of chloroform, the organic layer was separated, dried with sodium sulfate, and evaporated to dryness under vacuum. The residue was purified by sublimation at 130 °C and 0.01 torr. Yield: 38.86 g (86%). Melting point: 245–246 °C (lit. [13]: 245–247 °C).

^{1}H-NMR: ($CDCl_3$) δ/ppm 2.67(s)

^{13}C-NMR: ($CDCl_3$) d/ppm 54.51, 54.74. IR (KBr) 2961(w), 1444(m), 1317(s), 1214(m), 989(w), 847(s), 721(s) cm^{-1}.

1,3,5,7-Tetraphenyl-adamantane

Anhydrous aluminum chloride (250 mg, 1.9 mmol) was added to a solution of 1-bromo-adamantane (5.00 g, 23 mmol) and *t*-butylbromide (9.45 g, 69 mmol) in dry benzene (50 ml). The mixture was vigorously refluxed for 20 min in an oil bath. The reaction mixture was poured into ice water, ether was added, and the insoluble white solid was collected. For further purification the product was extracted with toluene for 6 days. Yield: 7.36 g (73%). Melting point: 404 °C (DSC) (lit. [14]: 403–404 °C).

Mass spectrum: M$^+$, $m/e = 440$.

IR(KBr): 3095(w), 3021(w), 2920(w), 2850(w), 1598(w), 1495(s), 1443(m), 1356(m), 1263(w), 1079(w), 1032(w), 762(s), 702(s) cm^{-1}.

$C_{34}H_{32}$: calc. C 92.68 H 7.32
found C 92.53 H 7.56.

1,3,5,7-Tetra-(*p*-biphenyl)-adamantane

A solution of 1,3,5,7-Tetrabromo-adamantane (10.00 g, 22.13 mmol) in 50 ml dry carbondisulfide was added slowly over a period of 1 h to a refluxing mixture of anhydrous aluminum chloride (2.95 g, 22.13 mmol) and biphenyl (150 g, 0.973 mol) in 150 ml dry carbondisulfide. After the generation of hydrogen bromide had stopped the mixture was refluxed and stirred for another 3 h. The mixture was allowed to cool to room temperature and hydrolyzed with 40 ml of diluted hydrochloric acid. The separated organic layer was washed with water, dried with sodium sulfate, and evaporated to dryness under vacuum. The excess of biphenyl was removed by distillation under reduced pressure at 130 °C. The residue was recrystallized from 150 ml of toluene. Yield: 1.50 g (9%).

^{1}H-NMR: ($CDCl_3$) δ/ppm 2.30(s), 7.35, 7.37(overlap d, t), 7.44(dd), 7.60, 7.62(overlap d, d).

^{13}C-NMR: ($CDCl_3$) δ/ppm 39.21, 47.39, 125.48, 127.01, 127.09, 127.16, 128.69, 139.14, 141.01, 148.35.

Mass spectrum: M$^+$, $m/e = 745$. IR(KBr) 3053(w), 3026(m), 2924(m), 2896(m), 2850(w), 1598(m), 1519(w), 1486(s), 1445(m), 1399(w), 1353(w), 1074(w), 1006(m), 837(m), 760(s), 734(s), 696(s), 564(w), 515(w) cm^{-1}.

$C_{58}H_{48}$: calc. C 93.51 H 6.49
found: C 92.83 H 6.70.

Thermal analysis

The thermal properties were investigated employing a Perkin Elmer DSC 7. The thermal analysis was carried out at a heating rate of 10 K/min.

X-ray investigations

Wide-angle x-ray scattering (WAXS) curves were obtained using a Siemens D-5000 diffractometer. Ni-filtered Cu-K$_\alpha$ radiation was used in all cases. The small-angle x-ray investigations were performed employing a Kratky compact camera equipped with a position sensitive detector.

Dielectric investigations

The dielectric analysis covered a frequency range from 20 Hz–1 MHz (Hewlett–Packard impedance analyzer HP 4284A. A nitrogen gas heating system controlled (within 0.2 K) the sample temperature in a temperature range from 100 to 650 K. The samples were kept between two electrodes (diameter 20 mm). The samples were heated up above the glass transition temperature before the upper electrode was brought in contact with the samples in order to obtain a homogeneous thin film with a good electric contact in the condenser. Spacers maintaining a defined separation of 50 μm were used.

Dynamical mechanical investigations

The dynamical mechanical properties were determined using the dynamical mechanical analyser produced by

Polymer Laboratories. It allows to determine the storage modulus and the mechanical loss over a broad range of temperatures for several frequencies.

Simulations on the shape of the multipodes

Direct experimental information on the actual shape of the multipodes both as a function of their chemical structure and of the temperature is not easily available. Electron or small-angle x-ray diffractions performed on diluted systems are possible means. Indirect information is available, for instance, from viscosity measurements and similar methods. We decided to evaluate the shape and rigidity at elevated temperatures using computer simulations.

These involved semiempirical quantum mechanical and force field calculations. The semiempirical quantum mechanical calculations were performed using the MNDO method, in particular the Austin Model 1 (AM1) and the Parametric Model 3 (PM3) [15]. The program Cerius 2 of Molecular Simulations Inc. was used to carry out molecular dynamic simulations. We selected Dreiding II as force field [16].

The semiempirical quantum mechanical calculations were used for the evaluation of the core structure and the rotational potential around the bond connecting the core unit and the arms. Force field calculations were performed to obtain the persistence length of the arms and thus a measure of their rigidity.

Figure 1 displays the shapes of a star-like system composed of an adamantane core and short arms consisting of 1 and 2 phenylene units (Scheme 1). It is obvious that the shape corresponds roughly to that of a star. Figure 2 shows the shape of the star-molecules for longer arms composed of phenyl units at various temperatures. It is evident that the arms become to a certain extent mobile at elevated temperatures. This increasing mobility is a favorable feature. It occurs at temperatures at which processing happens. This might facilitate processing without destroying the reinforcement effect: the mobility is reduced again on cooling to lower temperatures, i.e., in the solid state at room temperature.

The semiempirical quantum mechanical method was not only used to obtain an estimation of the actual shape of the molecules, it also provides a link to experimental results. The semiempirical quantum mechanical method allows to calculate, for instance, dipole moments and the polarizibility tensor. These data in turn allow to analyze optical and dielectric properties. This will be discussed below in more detail. Table 1 shows the dipole moments and polarizibilities for the molecules synthesized so far. The dipole is extremely weak as expected for the given chemical structure.

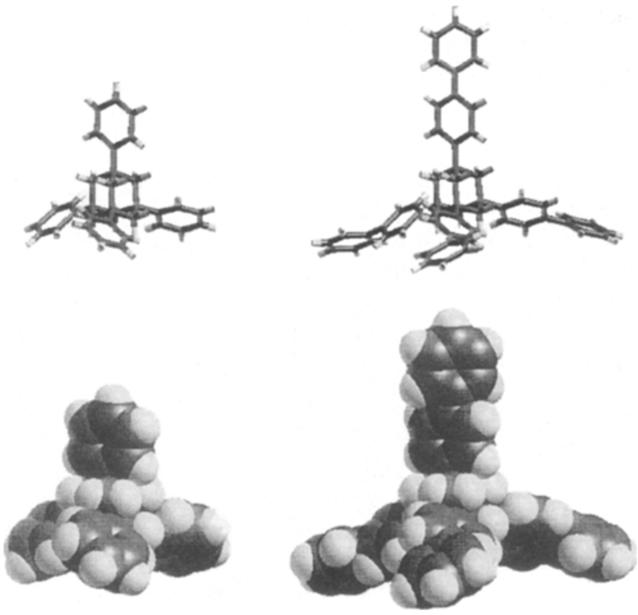


Fig. 1 Shapes of the adamantane-based multipodes with one and two phenyl units per arm

Fig. 2 Shapes of the adamantane-based multipodes with long arms at various temperatures (300 K, 500 K, 700 K)

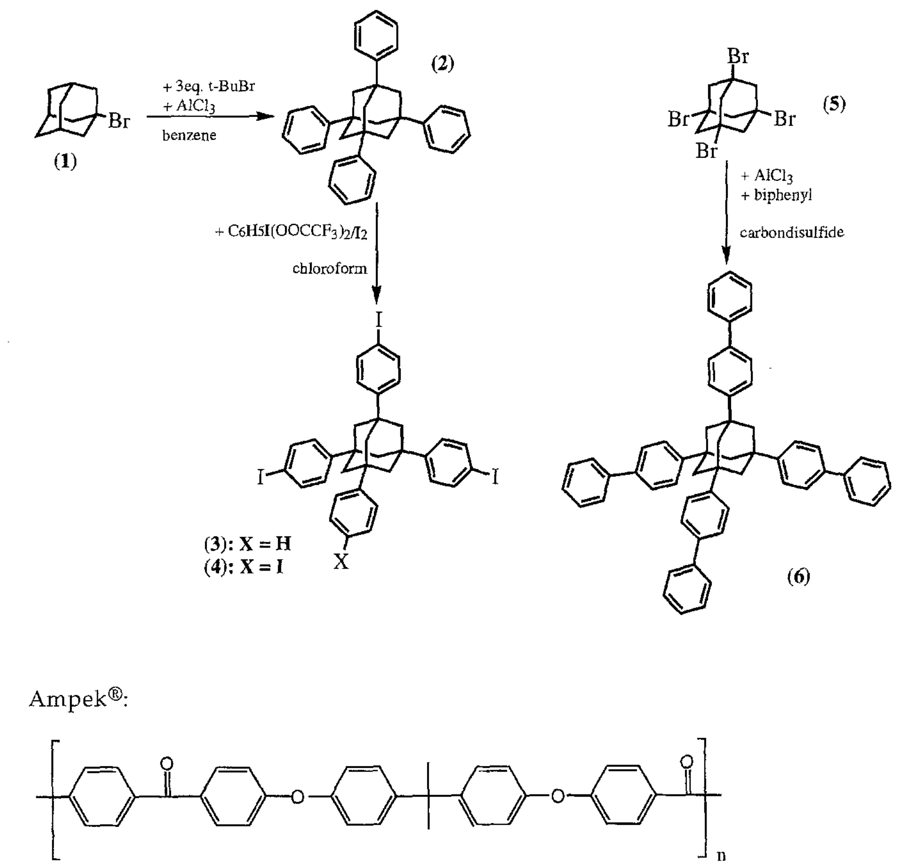
Synthesis of the adamantane-based multipodes

1,3,5,7-Tetraphenyladamantane **(2)**, the first generation of the star-like rigid multipode, was prepared by modification of a published procedure [17] (Scheme 1). 1-bromoadamantane **(1)** was converted with 3 eq. *t*-butylbromide in benzene into product **(2)**. **(2)** has a very low solubility in the normal organic solvents, including chloroform, THF and toluene. It is only soluble in boiling anisole, nitrobenzene or DMSO. In consideration of the low solubility of **(2)**, it is difficult to functionalize for the synthesis of further generations of the multipode. For example, **(2)** evades brominations and iodinations using standard methods [18, 19]. Only the reaction of the system (bis

Table 1 Dipole moments and polarizabilities for the adamantan derivatives

	dipole moment [Debye]	Polarizability [Å^3]
1,3,5,7-Tetraphenyl-adamantane	0.0154	58.8
1,3,5,7-Tetra-(*p*-biphenyl)-adamantane	0.0129	105.4

Scheme 1 Synthesis of the adamantane derivatives and the structure of Ampek



[trifluoroacetoxy]iodo)-benzene/iodine [20, 21] with **(2)** in chloroform led to a iodined product **(3)/(4)**. Unfortunately oligomer-GPC studies showed that there was a by-product of 10–20% consisting of the triiodide **(3)** or the meta isomer of **(4)**. This byproduct was difficult to remove, because it has a similar solubility to the main product **(4)**. After several recrystallizations from chloroform the amount of the byproduct was reduced to 3%. However, the loss in yield was very high. Another approach to the synthesis of the second generation of the multipode **(6)** is the direct Friedel–Crafts-alkylation of biphenyl with **(5)**. **(5)** was prepared from adamantane and bromine using a slight modification of a literature procedure [13]. Due to the inductive effect of the bromine substituents the generation of the carbenium ion in product **(5)** is reduced resulting in lower yields in the Friedel–Crafts-alkylation. We achieved yields only between 10–15%, but the purity of **(6)** after a recrystallization from toluene was very high (Fig. 3). The byproducts at a retention time of 14 h consist probably of substances, where two core molecules are combined.

Solubility

One of the motivations for considering such odd-shaped molecules was the theoretical prediction of an enhanced solubility in common solvents. The experimental finding is that these predictions are qualitatively correct. The solubility is found, for instance, to increase from 0.052 g/l to 10 g/l in toluene as the length of the arms is increased just by one phenyl unit.

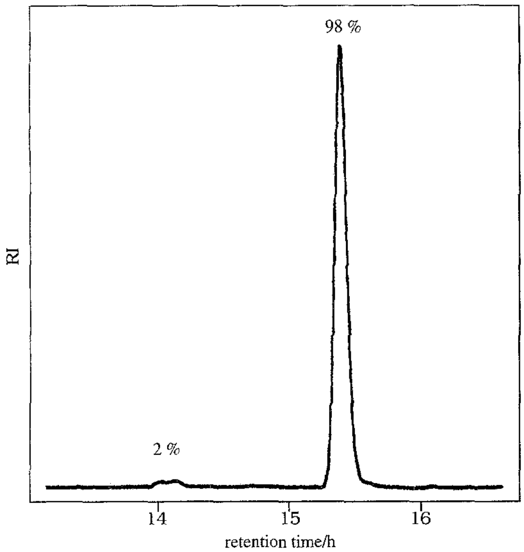


Fig. 3 Oligomer-GPC in THF of product (**6**)

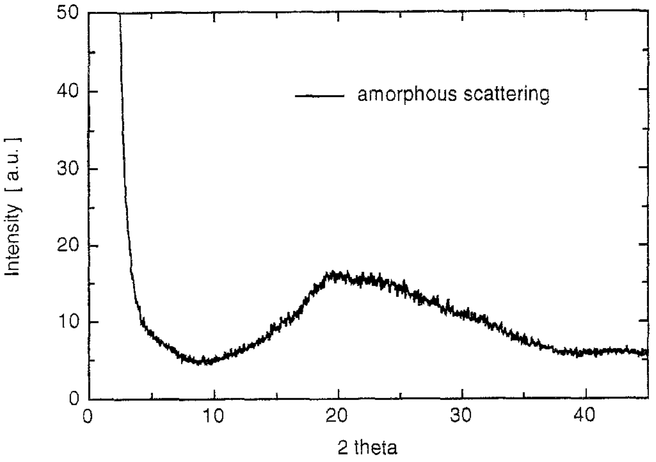


Fig. 4 Wide-angle diagram obtained at room temperature in the glassy state of the adamantane-based multipodes with one phenyl unit per arm

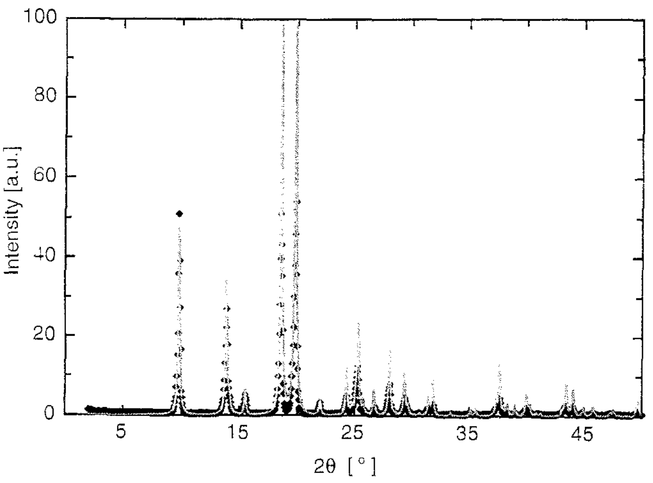


Fig. 5 Wide-angle diagram obtained at room temperature in the crystalline state of the adamantane-based multipodes with one phenyl unit per arm. Experimental data ◆; result of simulations -----

Structures displayed in the condensed state by the multipodes

Molecules possessing an odd shape may be envisioned to be unable to pack efficiently in the amorphous condensed state, to display thus a low density and to be unable to crystallize. These features are of general interest as far as the packing of odd-shaped particles is concerned but they are also of interest with respect to compatibility and molecular reinforcement. The compatibility is reduced by a strong tendency towards the formation of a liquid crystalline or crystalline state and a low packing density reduces the upper concentration limit of multipodes in the matrix to be reinforced.

At first we will discuss the packing density. Van Krevelen has shown that the ratio of the actual volume and the Van der Waals volume is always very close to 1.55 for the glassy state of a large number of chain molecules [22]. This value is also close to the one expected for the random close packing of spheres. To obtain information on the packing density, we thus determined the Van der Waals volume for the system containing two phenyl groups per arm from computer simulations. This value turned out to be 723.4 A^3. The density at room temperature was determined to be 1.143 g/cm^3. Using this value we find that the ratio observed for the multipodes amounts to 1.52. The obvious conclusion is that the star-like multipodes are able to pack very efficiently.

The x-ray analysis reveals that the systems discussed here can be quenched down from the melt into the glassy state provided they do not decompose prior to melting. The quenching becomes particularly easy as the branch length increases. The corresponding glass transition temperatures amount typically to 370–460 K.

The wide-angle x-ray diagram of the glassy amorphous state (Fig. 4) is characterized by the occurrence of asymmetric halos resulting probably from the superposition of two halos. Such a finding is not unusual for organic glasses. Two halos are expected to arise from intramolecular contributions as apparent from corresponding computer simulations on the radial distribution function, they reflect specific distances which occur with higher probability.

The x-ray analysis furthermore shows – in agreement with calorimetric studies – that the multipodes are able to crystallize from solution despite their odd shape. This is apparent from the x-ray data shown in Fig. 6 for the system with one phenyl group per arm. Similar results were obtained for the multipode with two phenyl units.

The small width of the reflections and the high number of reflections suggest that the order is highly developed. We were able to derive from the x-ray data the crystal structure for the multipodes with the arm length $n = 1$ and the distribution of the molecules within the cell. This was done using a powder indexing program to obtain a proposal for the unit cell. The unit cells turned out to be tetragonal with dimensions: $a = 12.78$ Å, $c = 7.18$ Å, 2 multipodes per unit cell, density: 1.25 g/cm^3. The check involved the construction of the cell using the program Cerius^2 (MSI), an energy minimization and the simulation of the corresponding powder diagram for the comparison (see Fig. 5).

The structure is characterized by a columnar type packing of the multipodes along the c-axis and a quadratic arrangement of the columns in the plane perpendicular to the column direction as shown in Fig. 6a, b. It seem possible that even multipodes with longer arms are able to crystallize with basically the same structure. Figure 6c shows the corresponding structure schematically. The prediction based on such an extrapolation is, however, that the density will decrease strongly if this kind of packing would continue to occur for longer arm lengths.

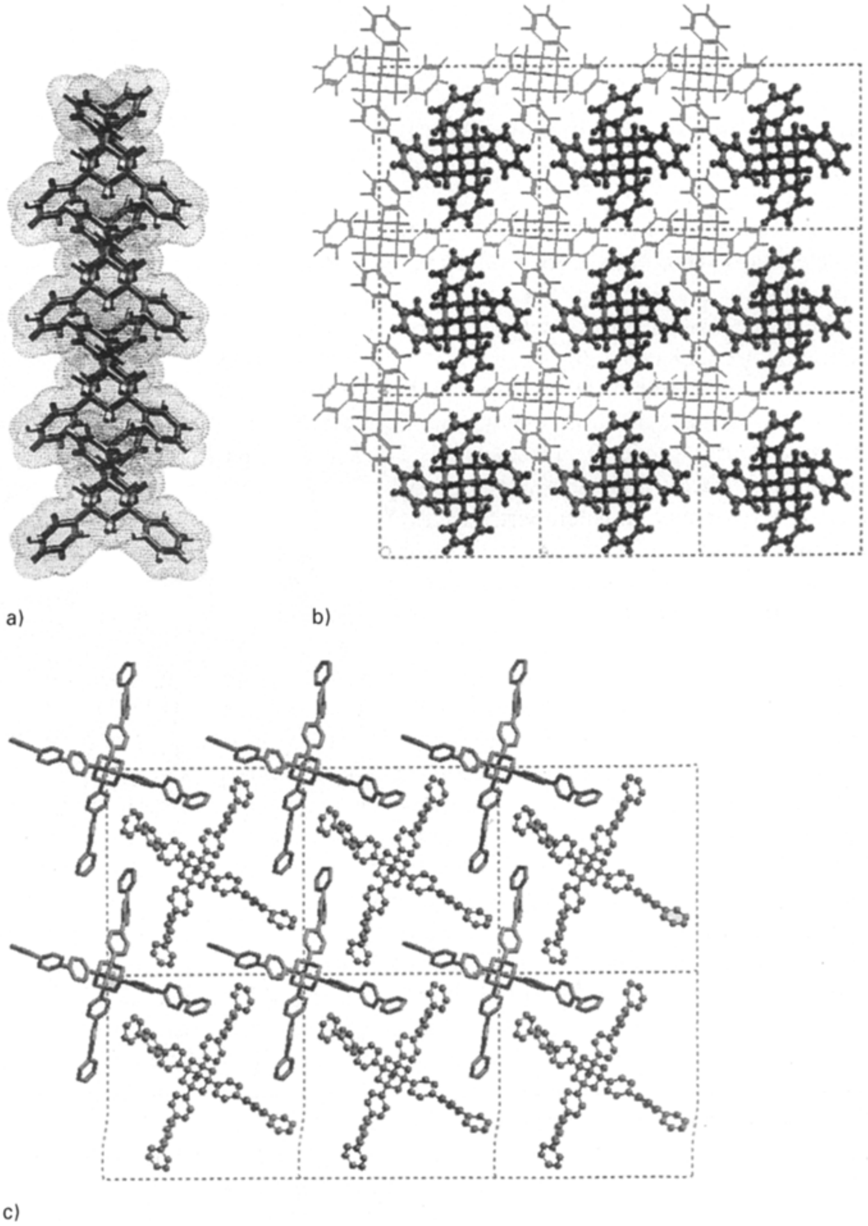


Fig. 6A, B Structure found for the adamantane-based multipodes with one phenyl unit per arm; **C** Structural model for the adamantane-based multipodes with two phenyl units per arm

Annealing allows to obtain and to freeze in partially crystalline states. Such a behavior is usually characteristic of polymer systems and reflects kinetic hindrances resulting from the restricted motions taking place in the condensed state.

So the general conclusion is that the odd shape and the rigidity of the star-like multipodes do not prevent them from developing a high degree of order in the condensed state.

Dynamics of the rigid star-shaped multipodes in their condensed state

Next, we will consider the mobility of the rigid multipodes in the condensed state as controlled by the internal mobility of the individual molecules and by intermolecular motions. The mobility in the condensed state is of interest first of all since the rigidity and shape of the molecules will severely restrict rotational and translational motions and secondly since an increasing internal mobility will enhance the compatibility but reduce the reinforcement effect. We have studied the dynamics using dielectric relaxation spectroscopy.

The molecules considered here possess very small dipole moments.

This is obvious from the results of MNDO-calculations displayed in Table 1. The dielectric studies shown in Fig. 7 reveal the absence of any indication of secondary relaxation in a broad frequency and temperature range. The dielectric constant is temperature and frequency independent, and no significant loss is detectable. Such properties are rather unusual and of technical interest.

The increase of the dielectric constant at high temperatures is connected with the glass relaxation. We have to conclude, however, that it is probably controlled by the onset of conductivity. The observed relaxation strength is far too large to be purely due to rotational motions of the multipodes. The agreement between the data obtained for the refractive index

$$n = 1.65; \quad n^2 = 2.7$$

and the data obtained for the dielectric constant even at high temperatures and low frequencies is good. This has to be taken as an indication that no relaxation processes contribute to the dielectric properties below the glass transition.

Rigid multipodes in polymer matrices

The state of dispersion depends critically on the preparation method. This is apparent from Fig. 8 which shows a mixture of 10 w% of a multipode in the polymer Ampek (see Scheme 1) prepared from solution. We see whiskers formed by the nucleation and growth of needle-like crystalline regions composed of the multipode.

Optically homogeneous transparent films can be obtained from such heterogeneous films by annealing at temperatures well above the glass transition temperature of the polymer matrix and the melting temperature of the

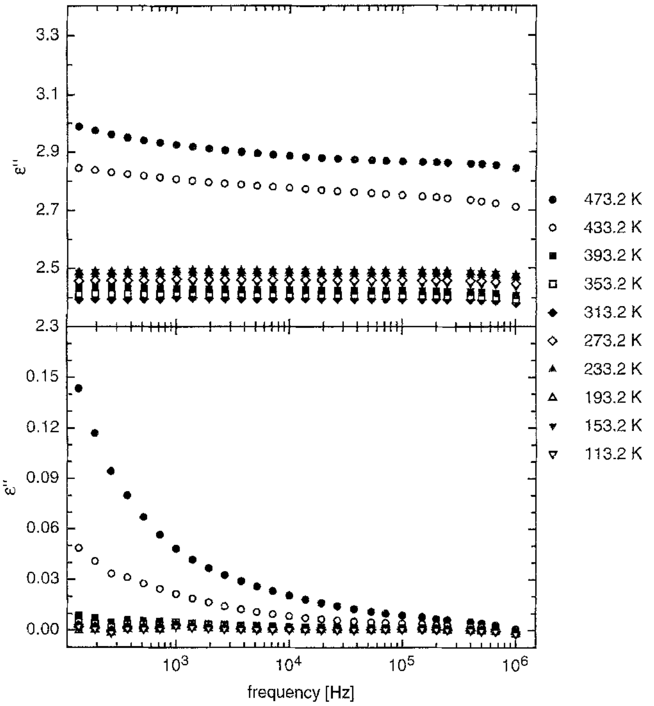


Fig. 7 Dielectric relaxation behavior of the condensed state of the multipode with two phenyl units per arm

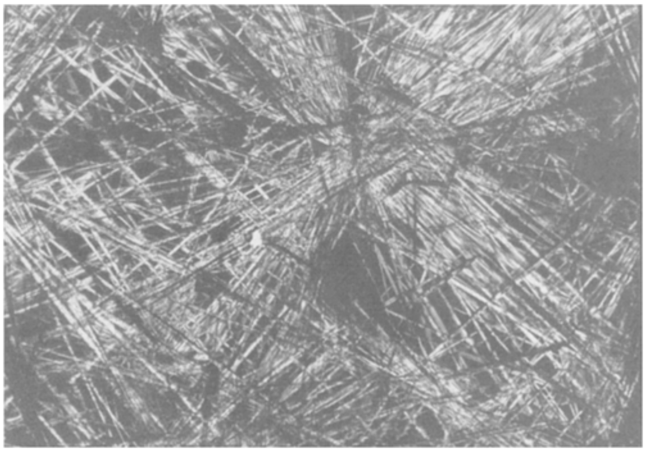


Fig. 8 Optical micrograph of a blend with multipode whiskers (10 w% of the adamantane-based multipode with two phenyl units per arm in a matrix of Ampek (see Scheme 1))

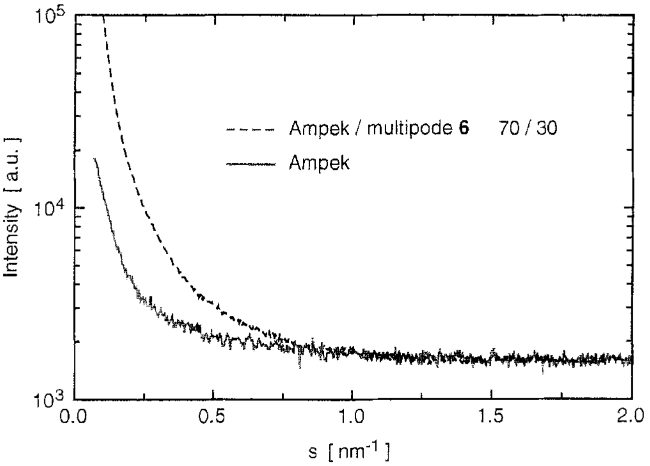


Fig. 9 Small-angle x-ray scattering curves of a polymer matrix (Ampek) and a blend of 30 w% of the adamantane-based multipodes with two phenyl units

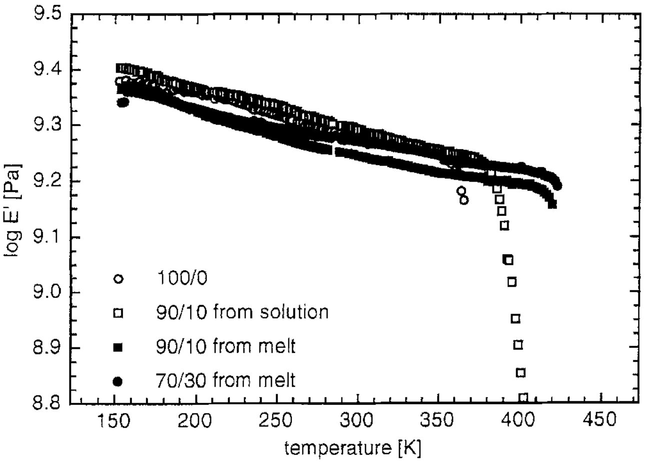


Fig. 10 Result of dynamical mechanical studies on the storage modulus of blends of Ampek with the adamantane-based multipodes with two phenyl units

multipodes. The small-angle x-ray investigation gave indications that, in fact, the mixture is homogeneous down to a molecular level. The small-angle scattering curves shown in Fig. 9 for the polymer matrix and a blend of 30 w% are very similar. We observe a slightly increased scattering at smaller scattering angles for the mixtures.

We found that the small excess scattering can be represented approximately by an exponential electron density correlation function

$$C(r) = e^{-r/\xi} ,$$

where ξ is the correlation length and r the distance between the sample volumes considered. This leads to an s dependence of $I(s)$ as described by Debye and Bueche [23, 24]. The correlation length obtained from the scattering curves is in the range of 2 nm. This is about the size of the multipode. So we conclude that such films do not show features at room temperature characteristic of a significant phase separation even at smaller scales. This is in agreement with the observation that only one glass temperature is observed in the mixture which decreases slightly with increasing concentration of the multipode.

Using a dynamical mechanical analyzer we studied the dynamical elastic modulus for the pure polymer film, the films containing the whisker structure and finally containing the multipodes homogeneously mixed with the polymer matrix. The results are shown in Fig. 10.

The storage modulus is found to be to a first approximation unchanged either by the presence of the whiskers or by the presence of the homogeneously distributed multipole. This holds for two different concentrations of the mixtures. No reinforcement effect is thus observed. This is actually not surprising in view of the very short arm length of the multipodes considered here. We know both from experiments and theoretical considerations that the arm length has to be increased strongly in order to be able to find reinforcement effects.

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