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Attempts to synthesize networks from rigid-rod oligomers

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Rigid-rod networks containing 2,5-dialkyl substituted *p*-phenylene chains have been synthesized, either by the palladium-catalysed coupling of boronic acid end-group oligomers with tribromo aryls, or by the reaction of hydroxy- or acetoxy-terminated oligomers with tricarboxy or tricarbonic acid chlorides. The reaction products were characterized by nuclear magnetic resonance and Fourier transform infra-red spectroscopies, and by dynamic mechanical analysis. As shown mainly by the dynamic mechanical analysis, solids of high modulus ($>10^7$ Pa) at a temperature higher than 300°C were obtained. Comparison of the behaviour of these solids with the properties of the starting oligomer or even with the linear analogue, shows that a high degree of crosslinking was achieved. Elemental analyses also support this view.

(Keywords: polymer networks; rigid-rod oligomers; characterization)

INTRODUCTION

The synthesis of networks in which the segments consist of rigid rod-like elements is a challenge to the synthetic chemist and a prerequisite to the test of theoretical predictions[1–3] on the behaviour of such networks. If such networks can be built with a random entanglement of the constituent rods, they are believed to behave as very high modulus solids[4]; in other words, the modulus is assumed to be related to the bending of the rods under a given load and not so much to the entropic elastic response of the network chains. Several attempts to synthesize such networks have been reported recently[3–9]. A recent review gives evidence of the different approaches to the experimental challenge of synthesizing reasonably well defined networks of this type[10]. In all cases known to us, the synthesis started from monomers which were subject to crosslinking during polycondensation. The monomers and crosslinkers were selected so as to arrive at a chain structure believed to show a certain molecular rigidity. Thus, the structures selected were all-aromatic polyamides[4,8,9], polyesters[4,8,9] or poly-*p*-phenylenes[5,6]. The insoluble and infusible reaction products were, however, difficult to characterize.

In the following, we report attempts to synthesize such rigid networks starting from oligomers or telomers which are crosslinked by reacting the end-groups with trifunctional monomers. This approach has not been used previously for synthesis of rigid-rod networks. Characterization of the resulting solids is attempted by solid-state nuclear magnetic resonance (n.m.r.), Fourier transform infra-red (*FT*i.r.) spectroscopy, thermal analysis and mechanical testing. The synthesis of the oligomers is based on our earlier work on the metal-catalysed coupling of phenylboronic acids to bromophenyl moieties providing structures containing poly-*p*-phenylene chains as the rigid element[11,12].

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EXPERIMENTAL

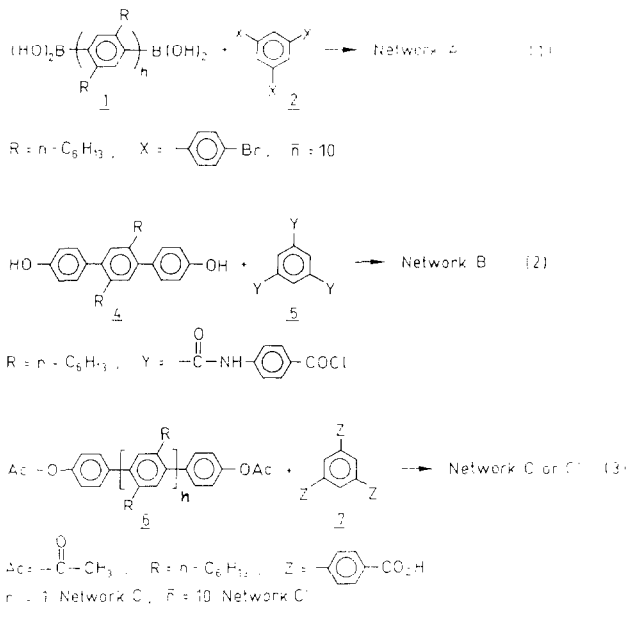
Materials and methods

The synthesis of monomers and telomers has been described elsewhere[12]. The crosslinkers **2**, **5** and **7** were synthesized following known procedures[4,13,14].

All solvents used in the polycondensation procedures were purified by distillation prior to use. ^{13}C cross polarization/magic angle spinning n.m.r. spectra were recorded by a Bruker AC 300 spectrometer. *FT*i.r. spectra were obtained by a Nicolet 60 SC spectrometer. The mechanical data were obtained using a Rheometrics RMS 800 instrument.

Synthesis of the network structures (reactions (1)–(3))

Network A. 4-Bromo-2,5-dihexyl phenylboronic acid (0.960 g, 2.6 mol) and 0.145 g (0.44 mmol) of 2,5-di-n-hexyl-bis-phenylboronic acid were reacted together in the presence of dichloro[1,1′-bis(diphenylphosphino)ferrocene] palladium [$PdCl_2$ (dppf)] under an inert atmosphere in a reaction medium consisting of 16 ml tetrahydrofuran (THF) and 3.0 ml of NaOH (3 N) in order to obtain the oligomer **1** after having refluxed the mixture for 3 h. Network A was obtained by adding 110 mg of **2** dissolved in 3 ml of THF to the black reaction mixture. After 2–3 min the mixture gelled and stirring was ceased. Heating was continued for 48 h, then the gel was cut into small pieces and thoroughly washed with THF to remove the soluble fraction, and was finally dried *in vacuo*. Yield was 99%. Elemental analysis, found (calculated): C 88.59 (89.02), H 10.67 (10.98), Br 0.2. The average degree of polymerization $\bar{n}$ of the oligomer **1** produced *in situ* was



determined from a sample prepared in parallel under exactly the same conditions. Details of the analysis have been described elsewhere[12].

Network B. A sample (0.5 mmol) of **5** was prepared by treating the corresponding carbonic acid with $SOCl_2$ at reflux for 24 h. The excess of $SOCl_2$ was distilled off from the clear solution and the remaining solid was dried. A sample (0.75 mmol) of **4** was added together with 5 ml of sym. tetrachloroethane and 0.7 ml pyridine. The mixture was heated at 110°C. The clear solution gelled after 5 min. The heating was continued for 2 h. $CHCl_3$ was added and the solvent replaced several times. The combined $CHCl_3$ fractions were evaporated and, after washing with water and drying, the soluble fraction was obtained. The gel was dried in high vacuum at 150°C until it reached constant weight. Swelling experiments were performed in toluene and the results are shown in *Table 1*.

Networks C and C'. A sample (0.96 mmol) of **6** was placed together with 0.64 mmol of **7** in a reaction vessel and the mixture was melted under N_2 using a metal bath at 260°C. The melt was stirred for 30 min when the stirring ceased. Heating was continued for 2 h. Then vacuum (0.1 mbar) was applied for 2 h at 260–280°C. The product was swelled and extracted by toluene for the determination of the soluble fraction and also the rate of swelling. The polymer was dried in high vacuum at 150°C until constant weight. The results are shown in *Table 1*. The yield was quantitative. Elemental analysis of network C, found (calculated): C 83.29 (83.93), H 6.62 (6.75)

Table 1 Data concerning the synthesis and swelling behaviour of networks A, B and C

Network typw	Starting oligomer	Length of network chain[a]	Yield (%)	Soluble fraction (%)	Swelling ratio, r
A	**1**	10	98	0	4
B	**4**	3	100	10	4
C	**6**	3	100	0	0.5
C'	**6**	10	99	10	[b]

[a] Degree of polymerization of the functional oligomer
[b] Not precisely measured

Mechanical analysis

The powdery product was pressed to form a pellet which was designed to be inserted into the parallel plate rheometer. The pellet was fixed between the parallel plates using an epoxy glue. The same procedure was performed with the oligomer for comparison. In the case of network C, a piece of the glassy reaction product was cut to fit between the plates of the rheometer

RESULTS AND DISCUSSION

Polymer synthesis

We can divide the synthesized products into two categories: (a) networks formed from statistical oligomers with an average degree of polymerization (DP_n) of about 10 (e.g. networks A and C'); (b) networks with short segments (terphenylene units) between crosslinkers (e.g. networks B and C). Two different types of reaction were used for the connection of the reactive oligomers with the crosslinking reagents. Aryl–aryl coupling was the first choice in order to have the same kind of bonds at the crosslinking points as in the oligomeric segments. Among the different possibilities, the palladium-catalysed coupling (using $PdCl_2$(dppf)) of the boronic acid end-group oligomers with tribromo benzene derivatives was chosen. The second possibility was the crosslinking of the hydroxy-terminated oligomers or telomers with tricarboxy compounds forming an ester-type bond at the crosslinking sites.

Polyphenylene-type networks. Network A belongs to the polyphenylene-type networks and also the non-gelled product derived from oligomer **1** and 1,3,5-tribromobenzene obtained under identical polymerization conditions. The second product did not form a gel after 2 days, probably because of kinetic effects in the polycondensation due to steric hindrance. No further examination was made for that product. Network A was synthesized in very high yield. After the addition of the crosslinking agent, the mixture gelled within 2–3 min and filled the whole reaction vessel. To determine whether a soluble fraction was present, the material was equilibrated with various solvents such as THF, toluene and phenyl acetate. No change in weight was observed after such treatment. The presence of rigid fractal polymer fragments cannot be excluded based on this result. However, it should be emphasized that the starting oligomer was very soluble in the solvents used to determine a possible presence of the soluble fraction. Also, hyperbranched polyphenylenes of relatively high molecular weight are very soluble in common organic solvents[6]. We note that the present system does not give rise to specific interactions such as hydrogen bonding, which would help the trapping of fractals in the network structure formed. Thus, it seems quite unlikely that fractals, instead of an 'infinite' network, could be formed in the present case.

Polyester-type networks. The reaction of the hydroxy end-group oligomers and telomers with tricarbonic acid chlorides was an alternative approach to the formation

of highly crosslinked networks. Products B, C and C' were synthesized by that method. In relation to the gelation behaviour, only product C filled the whole reaction vessel and did not give rise to a soluble fraction after extraction, as shown in *Table 1*. In the other two cases, significant amounts of soluble fractions were obtained. Especially in case B, where the monodisperse diol **4** was used, the large amount of soluble fraction can be attributed to the side reactions of the tricarboxy compound during treatment with thionyl chloride, as shown by ^{13}C n.m.r. spectroscopy.

Polymer characterization

The first examination of the synthesized polymers was the determination of the soluble fraction, as discussed above, and the swelling ratio in toluene. The swelling ratio was determined from the weight difference between the swelled and the dried polymer normalized with regard to the weight of the dried polymer. The results obtained are shown in *Table 1*. From all examined products, network C shows a very low swelling ratio, as expected for a real rigid-rod network. In the case of product A, the higher swelling ratio is possibly due to the presence of a significant amount of alkyl chains attached to adjacent benzene rings forming an environment which could, in principle, absorb organic solvents. It could also be attributed to the presence of some defects in the network structure. Product C' also shows a considerably higher swelling ratio, much higher than that of network C prepared from the same diol; however, this, together with a high soluble fraction, is attributed to the defects caused by the imperfect crosslinker as discussed before.

Further characterization was carried out only for polymers A and C, the behaviour of which is in accordance with that expected for networks consisting of rigid rod-like segments connected by stiff branch points.

Elemental analyses for networks A and C are given in the Experimental section and are in fairly good agreement with the calculated values. It should be noted that because of the intractable nature of the desired products, purification was a very difficult task. In the case of network A, the reaction extent could be tested by the determination of unreacted bromo end-groups. According to our previous experience[12], the DP_n values obtained from end-group analysis in the case of oligomers with bromo end-groups were in very good agreement with data based on n.m.r. analysis. The bromine content dropped from the initial value of 6 wt% in the starting reaction mixture, to 0.2 or 0.5% for the two different runs. Based on these values, an extent of reaction of 97% was calculated for the system having the lower bromine content.

The solid-state ^{13}C n.m.r. spectrum of network A is shown in *Figure 1a* in comparison with the spectrum of the oligomer **1** (*Figure 1b*). It gives clear evidence of the incorporation of the oligomer chains into the network and the formation of further aromatic carbons at the crosslinking sites.

*FT*i.r. spectra of the boronic ester end-group oligomer and of network A are shown in *Figure 2*. Comparing these two spectra, we can see the disappearance of the absorption at 1328 cm^{-1} due to the B–O bond in the network, while a new absorption at 835 cm^{-1}, due to the 1,3,5-trisubstituted ring[6,15], appears in this product. Also,

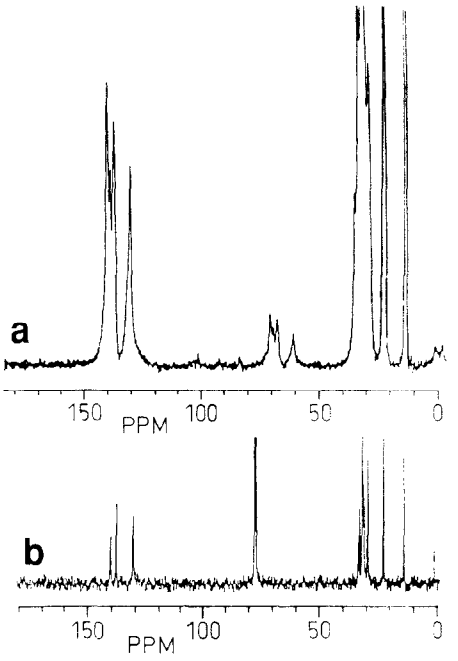


Figure 1 Solid-state ^{13}C n.m.r. spectra of network A (a) and the *p*-phenylene oligomer **1** (b)

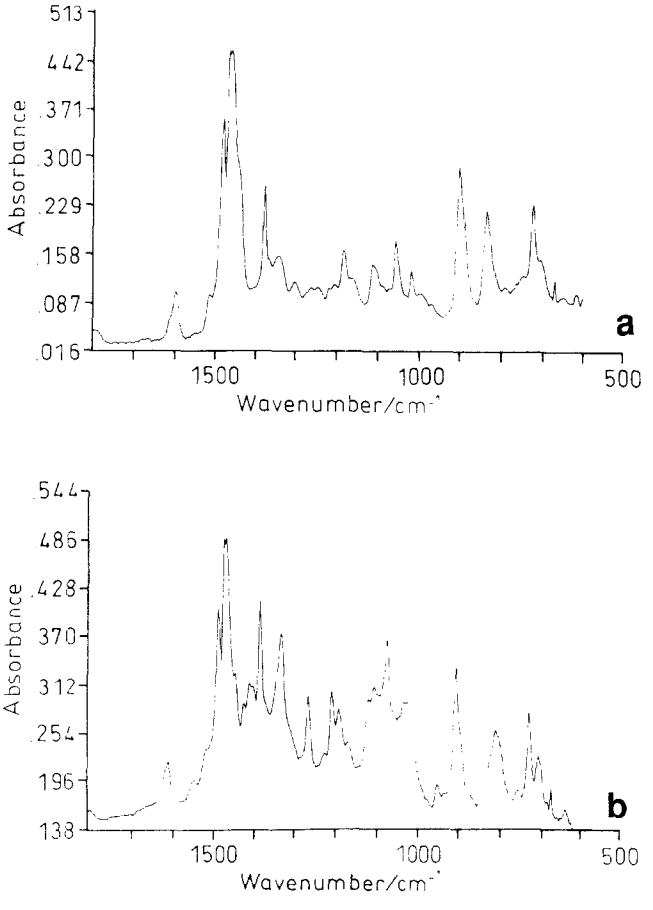


Figure 2 *FT*i.r. spectra of network A (a) and oligomer **1** (b)

the region of 1072–1068 cm^{-1}, were the *p*-arylbromide absorbs, is free of such a peak in the spectrum of the network.

The spectrum resulting from examination of network C by solid-state ^{13}C n.m.r. is shown in *Figure 3a* in comparison with the ^{13}C high resolution spectrum of

monomer **6** (*Figure 3b*). The appearance of an aromatic carbon connected to an ester oxygen at 160 ppm and the carboxylic carbon at 164 ppm are clearly shown. This last peak, in combination with the absence of any peak at 170 ppm where the carbonyl carbon in the diacetoxy monomer **6** appears, supports the high degree of conversion to the network. The signal of the carbonyl carbon in substituted polyesters has been found[16] at 161.5 and 165 ppm, in very good agreement with our results. The *FT*i.r. spectrum of network C (not shown) supports the presence of the ester bonds by the very strong absorption at 1738 cm^{-1} due to the ester carbonyl. The spectrum did not show evidence for other types of carbonyl groups or for free carboxylic residues.

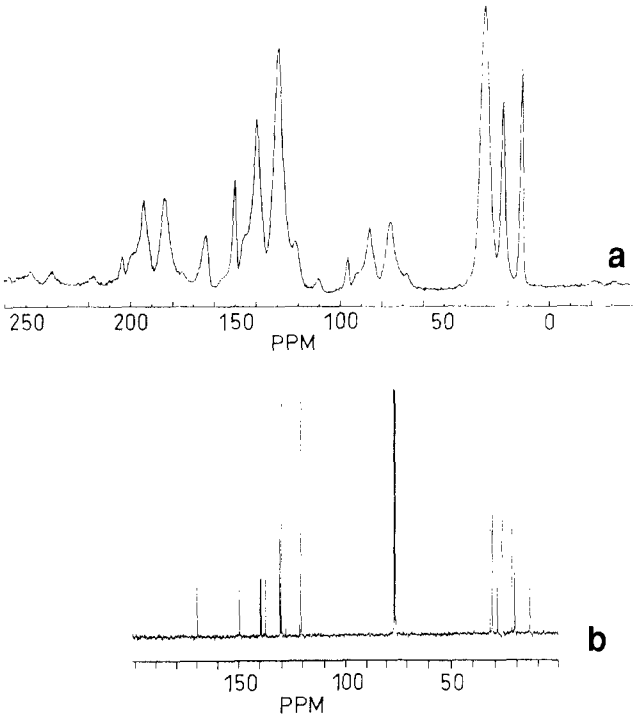


Figure 3 Solid state ^{13}C n.m.r. spectra of network C (a) and monomer **6** (b)

Thermal analysis has also been done by means of differential scanning calorimetry (d.s.c.) and thermogravimetric analysis (t.g.a.). D.s.c. thermograms of networks A and C did not show any first or second order transitions until 350°C where the thermal decomposition started. It is interesting to note that the oligomers with $DP_n \approx 10$ show a sharp melting peak at around 260°C.

The t.g.a. traces for networks A and C show two stages of thermal decomposition. The first is related to the elimination of the aliphatic side chains at around 450°C, and the weight loss during this process is in good agreement with the weight percentages of the aliphatic chains in each product. The second stage is very broad and extends from 500°C to above 800°C.

X-ray analysis of network A shows a drastic reduction of the intensity of the Bragg peaks due to the crystalline structure of oligomer **1**. This result supports the disordering introduced by the crosslinking reaction.

Dynamic mechanical analysis

A further characterization of the networks was attempted by dynamic mechanical analysis. The results for network A are shown in *Figure 4a* in comparison with oligomer **1** (*Figure 4b*). The loss modulus G'' of network A shows two maxima, one at low temperatures (below −50°C) and the other at about 100°C. Both are observed in the spectrum of the linear dialkyl-substituted polyesters[17,18]. These processes were assigned as secondary transition due to the presence of the aliphatic side chains. With increasing temperature, G' shows a plateau until the highest measured temperature (330°C).

In the case of network C, G' show a plateau in the temperature range 200–300°C with a value of about 10 MPa, which is also the case for the linear polyester[17]. At higher temperatures, the linear analogues show a sharp decrease of the modulus E' while the networks prove to be insensitive with regard to the temperature changes.

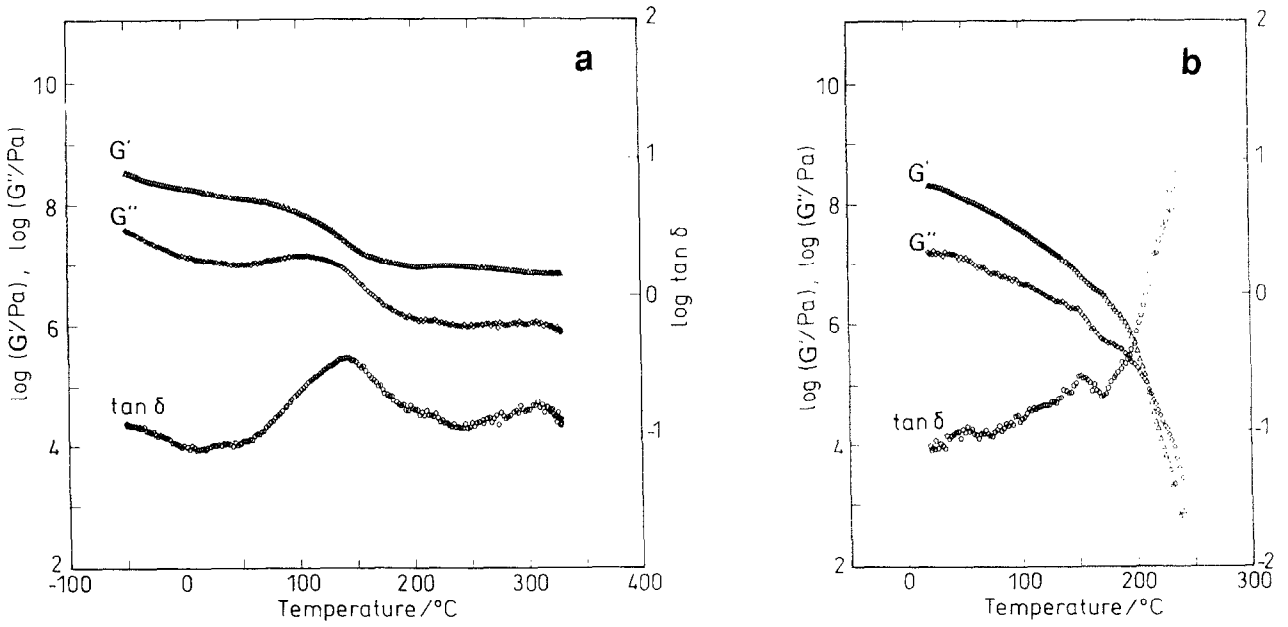


Figure 4 Dynamic mechanical spectra of network A (a) and oligomer **1** (b)

The plateau modulus of the examined networks was located at about 10 MPa. This value is one order of magnitude higher than that predicted for flexible networks, and supports the view that the synthesized products have an unusual structure. The temperature dependence of the modulus of our products is in good agreement with the expectation[4] that the modulus of such rigid networks will not be significantly reduced with temperature. The only difference from expectation is in the region of 50–150°C where transitions and relaxation processes, due mainly to the presence of side chains, are observed.

As realized in this study, problems arising from the nature of the materials involved are quite difficult to overcome. A very high degree of reaction cannot be achieved due to the fact that functional groups located at distant sites cannot approach each other because of the rigid nature of the network. Fractals, probably formed under conditions of a lower degree of conversion, are difficult to extract because they may be entrapped in the rigid network structure. Finally, specimens in a form desirable for mechanical measurements are difficult to prepare.

CONCLUSIONS

Rigid networks can be synthesized either by using the palladium-catalysed coupling of boronic ester end-group oligomers of poly-*p*-phenylene desired structures and aromatic tribromo crosslinking reagents, or by hydroxy-terminated oligophenylenes and tricarboxy crosslinkers. These products have been characterized by elemental analysis, n.m.r. and *FT*i.r. spectroscopies, and thermal and dynamic mechanical analyses. The swelling ratio of some products is very low, as expected for that kind of material, and the soluble fraction was zero for some preparations. Dynamic mechanical analysis showed effective crosslinking by comparison of the modulus of the networks with that of the starting oligomers. Products showing unusual behaviour, with high modulus at high temperatures, were obtained.

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