Synthesis and Characterization of Rod−Coil Poly(amide-*block*-aramid) Alternating Block Copolymers

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ABSTRACT: A series of block copolymers that contain rigid liquid crystal forming blocks of poly(*p*-phenylene terephthalamide) (PPTA) and flexible blocks of hexamethylene adipamide (PA 6,6) have been synthesized. The polymers have been prepared in a one-pot procedure by addition of PA 6,6 monomers to an amine-terminated PPTA oligomer via a low-temperature polycondensation reaction in *N*-methyl-2-pyrrolidone. Via this method block copolymers are formed that were characterized by inherent viscosity measurements, size exclusion chromatography (SEC), NMR, Soxhlet extraction, and TGA. The molecular weights of the synthesized rod−coil block copolymer materials are estimated from their intrinsic viscosities by a semiempirical model that combines both the intrinsic viscosity relations of the homopolymers and the mean-square end-to-end distance of the rod−coil copolymer.

Introduction

The study of block copolymers containing rigid liquid crystal forming segments is of great interest both from a scientific and from a technological point of view. Monodisperse rod−coil diblock copolymers have served as a model system to examine both theoretically[1−5] and experimentally[6−9] the self-assembly resulting from the interplay between liquid crystalline (LC) ordering and microphase separation. Because both processes compete during the minimization of free energy, morphologies that are distinctly different from flexible block copolymers will be obtained, showing LC order at a molecular scale together with long-range organizational order. From a technological point of view monodisperse rod−coil block copolymers offer numerous opportunities for designing nanostructured materials in a wide field of applications. In particular, rod−coil block copolymers bearing a conjugated segment as the rod block received great interest and have been proposed for electrooptic and photonic devices.[10−12]

The phase behavior of rod−coil diblock (and multiblock) polymers with a broad molecular weight distribution is much less understood, and up to now there are no theories available describing the phase behavior of such materials. Over the past two decades numerous publications have appeared dealing with synthesis and characterization of polydisperse multiblock copolymers comprised of alternating rigid, liquid crystal forming, and flexible (amorphous or crystalline) segments. A considerable amount of research on LC multiblock copolymers has been done in the field of thermoplastic elastomers where LC segments replace the hard segments of conventional thermoplastic elastomers. Several publications are available that deal among others with LC poly(ether−ester),[13] poly(ether−amide),[14,15] and polyurethane[16] block copolymers where the rigid segments are polyurethane blocks and the flexible segments are usually polyether or polyester blocks.

Block copolymers containing LC segments can also be considered as a molecular composite. The concept of a molecular composite was introduced in the early 1980s by the groups of Takayanagi[17] and Helminiak,[18] and the concept can be defined as a homogeneous dispersion of rigid polymer microfibrils of high aspect ratio in a flexible coil polymer matrix in order to improve the mechanical and physical properties of the matrix polymer. These materials can be seen as an interesting alternative for conventional fiber reinforced composites. The main drawback observed in preparing molecular composites is the incompatibility between the rigid and the flexible polymer. Because of this incompatibility, the rigid polymer tends to phase separate in macroscopic aggregates, causing the reinforcement effect to a large extent to be lost. An alternative approach is to prepare a block copolymer composed of rigid and flexible segments. Because of the covalent bond between the different segments, phase separation on macroscopic scale is prevented. On the basis of this principle, Takayanagi[17] prepared block copolymers of a flexible aliphatic polyamide PA 6 (commercial name nylon-6) or PA 6,6 (nylon-6,6) with a rigid aromatic polyamide poly(*p*-phenylene terephthalamide) (PPTA, commercial names Kevlar and Twaron) or poly(benzamide) (PBA). Takayanagi showed that PA reinforced with the block copolymer displayed improved mechanical properties compared to a corresponding blend of the aramid and PA.

In the present study we report the synthesis and characterization of poly(amide-*b*-aramid) multiblock copolymers, which are likely to show LC phases in sulfuric acid. Block copolyamides with other, but comparable, rigid and flexible segments have been synthesized which are able to show a LC phase if a sufficient amount of rigid units is incorporated in the copolymer.[19−22] In contrast to the molecular composite approach, phase separation on a macroscopic scale will not occur, and local microphase separation may induce coil stretching of the flexible segments giving rise to an extended modulus of the materials. In addition, we want to gain insight into the evolution of the microstructure of such materials as a function of composition and processing conditions also in relation with the macroscopic mechanical properties. We believe that the structure of this type of block copolymers, at least conceptually, may be compared to the structure of dragline silk. This type of block copolymer should therefore display high-energy absorption because of the combination of rigid aramid blocks providing stiffness and amor-

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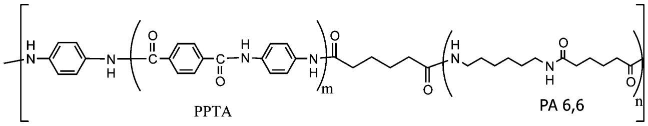


Figure 1. Chemical structure of a PPTA-*b*-PA-6,6 block copolymer.

phous polyamide blocks providing elasticity. Basically this approach can be seen as a reversal of the general perspective; i.e., we are not aiming to improve the properties of PA with PPTA as reinforcement (molecular composite approach), but we want to modify PPTA with PA aiming to enhance the impact resistance of PPTA by introducing more elasticity and to obtain higher fracture energy.

In this study we will focus on the block copolymer composed of alternating PPTA and PA 6,6 blocks, similar to those originally reported by Takayanagi,[17] although the polymerization route has been slightly altered. Takayanagi prepared copolymers via the Morgan[23] route which makes use of HMPA as a cosolvent. This solvent is known to be carcinogenic; so therefore the synthesis route of our choice is the Vollbracht[24] route, and the solvent is a mixture of NMP/$CaCl_2$. The block length can be altered easily by adjusting the ratio of the monomers. Takayanagi synthesized the block copolymer from an acid−chloride PPTA oligomer. We have prepared our block copolymers from an amine-terminated oligomer because amine end groups tend to be more stable in the solvent mixture. The chemical structure of a repeat unit of the prepared block copolymers is shown in Figure 1.

Experimental Section

Materials. *N*-Methyl-2-pyrrolidone NMP (Acros) was vacuum-dried over CaH_2 and stored on molecular sieves. Terephthaloyl chloride TDC (Acros), phenylenediamine PDA (Acros), and hexanediamine HAD (Acros) were purified by vacuum sublimation before use. Calcium chloride (Boom) was dried overnight under vacuum at 200 °C. Triethylamine (TEA, Merck) was distilled over CaH_2 and stored over molecular sieves. Adipoyl chloride (AC, Fluka) was purified by vacuum distillation.

Measurements. The block copolymers were extracted in a Soxhlet apparatus using formic acid, which is a solvent for PA 6,6, but a nonsolvent for PPTA. In each case, 3 g of polymer was exposed to 80 mL of formic acid and extracted for 24 h. Next the unextracted part was filtered. The extracted part was precipitated in ethanol and then filtered. Both the extracted and unextracted part were washed with water and dried under vacuum at 50 °C. ^1H NMR spectra of the polymer specimen in D_2SO_4 were obtained with a 400 MHz UR-400S Varian spectrometer.

The inherent viscosities (η_{inh}) of the polymers were determined with an Ubbelohde viscometer. For all polymers a 0.5 g dL^{-1} solution in concentrated sulfuric (96 wt %) acid at 30 °C was used. The intrinsic viscosities [η] of the polymers were determined by extrapolating the reduced viscosities (η_{sp}/c) obtained at four different concentrations (0.2, 0.3, 0.4, and 0.5 g/dL) to zero concentration. Size exclusion chromatography (SEC) analysis of the samples was performed at Teijin Twaron Arnhem. The polymers were dissolved in concentrated sulfuric acid (0.1 mg/mL) which was used as the mobile phase and separated by SEC using a Zorbax GPC column (250 × 6.2 mm). For detection a UV detector at 340 nm was used. The molecular weight values were calculated using Cirrus version 1.1 GPC software (Polymer Laboratories). As a reference, a high-MW Twaron (PPTA) yarn type 1010 and a PPTA trimer were used.

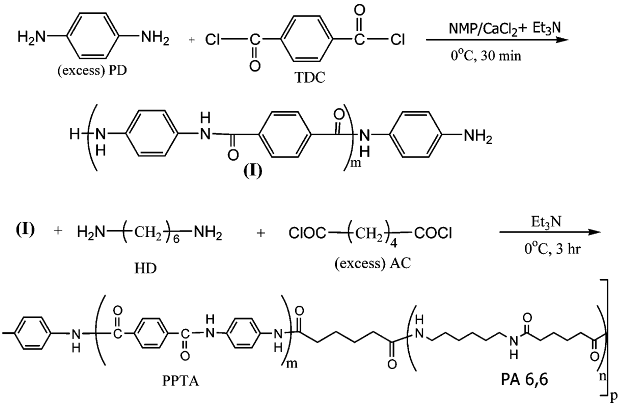
Thermal gravimetric analysis (TGA) in nitrogen was performed with a Perkin-Elmer 7a using a heating rate of 10 °C/min. Differential scanning calorimetric (DSC) measurements were performed with a Perkin-Elmer TAC 7/DX DSC using a heating rate of 10 °C/min.

Table 1. Inherent Viscosities and Compositions of Block Copolymers and Oligomers

polymer	η_{inh} (dL g^{-1})[a]	amount of flexible (PA 6.6) block (mol %)	no. of repeat units[b] of	
			PPTA *m* (−)[c]	PA *n* (−)[c]
P10-4	1.87	29	10	4
P10-10	1.71	50	10	10
P4-4	2.06	50	4	4
P4-10	0.75	71	4	10
P4-0	0.42	0	4	0
P10-0	0.76	0	10	0
P0-4	0.22	100	0	4
P0-10	0.39	100	0	10

[a] Measured at a concentration of 0.5 g/dL in 96% H_2SO_4 at 30 °C. [b] The number of repeat units based on stoichiometry using Carothers' equation. [c] *m* and *n* refer to Figure 1.

Scheme 1. Synthetic Scheme for the Synthesis of PPTA-*b*-PA-6,6 Multiblock Copolymer



General Procedure for the One-Pot Block Copolymer Polycondensation Reaction. A typical block copolymerization experiment was performed as follows: in a four-neck reaction vessel equipped with a mechanical stirrer and a dropping funnel under an argon atmosphere, 6.00 g (0.0556 mol) of PDA was placed in a mixed solvent of 22 mL of TEA and 200 mL of NMP containing 22 g of $CaCl_2$, which was partially in the solid state. After the mixture was cooled in an ice bath to 0 °C, 9.02 g (0.0444 mol) of finely powdered TDC was added to the solution under vigorous stirring. The solution was kept in an ice bath for 30 min to obtain a clear dark yellow fairly viscous solution containing an amino-terminated PPTA oligomer. To this mixture was added successively 5.16 g (0.0444 mol) of HAD, 18 mL of TEA, and 100 mL of NMP. To this solution 10.17 g (0.0556 mol) of AC was added dropwise. AC was added dropwise to the mixture because by slowly adding the last part of the AC reactant to the mixture the system is able to slowly pass through the stoichiometric equilibrium. The reaction mixture was kept in an ice bath for 1 h and at room temperature for another 2 h to obtain a viscous gel. This gel was precipitated into a large amount of water, blended in a blender jar, repeatedly washed with water, and dried under vacuum at 50 °C. According to this method a random block copolymer is prepared that consist of 50 mol % PPTA and 50 mol % PA 6,6. The theoretical degree of polymerization of the individual blocks is 9, and the polymer is denoted as **P4-4** where the numbers refer to the number of repeat units of respectively the aramid and aliphatic amide blocks (*m* and *n* in Figure 1). By simply varying the monomer ratio according to Carothers' equation, every desired composition can be made. We have synthesized four different types of block copolymer, i.e., **P10-4**, **P4-4**, **P10-10**, and **P4-10**. The composition and inherent viscosities $[\eta]_{inh}$ of the copolymers and the aramid and polyamide prepolymers are given in Table 1. The synthesis route of the copolymer is schematically shown in Scheme 1. The inherent viscosities are measured at a concentration of 0.5 g/dL in 96% H_2SO_4 at 30 °C.

Table 2. Copolymer Compositions Calculated from ^{1}H NMR Analyses and Extraction Results

polymer	weight fraction of PA 6,6 repeat units in copolymer by stoichiometry	weight fraction of PA 6,6 repeat units in copolymer by NMR analysis	amount extracted by formic acid (wt %)
P10-4	0.29	0.35	0
P10-10	0.49	0.55	0
P4-4	0.49	0.60	0
P4-10	0.69	0.76	16.7
P4-10 (extracted part)[a]	NA	0.87	NA

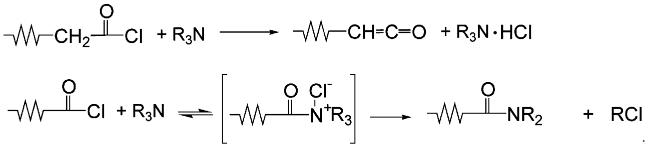
[a] Extraction with formic acid in a Soxhlet apparatus.

Table 3. Molecular Weight of the Copolymers As Obtained by SEC and Viscosimetry

polymer	[η] (dL/g)	$M_{\mathrm{v,copolymer}}$ [a]	M_n	M_w	PDI
P10-4	2.16	9200−16100	3600	11000	3.1
P10-10	1.99	11000−17700	3600	11600	3.2
P4-4	2.44	9800−23600	5500	17200	3.2
P4-10	0.94	5500−7300	2900	7200	2.5
P4-0	0.46	2800	800	2100	2.6

[a] $M_{\mathrm{v,copolymer}}$ values calculated from eq 13 with α range of 0.69−1.09; M_v value for **P4-0** from the Mark−Houwink equation for PPTA.

Scheme 2. Side Reactions of Acid Chlorides with Tertiary Amines



Results and Discussion

Polymer Synthesis. The synthesis of this type of aromatic−aliphatic block copolyamides by the low-temperature solution method is rather complex. The feature that complicates the synthesis is that during the polymerization hydrogen chloride is released which can react with the diamine reactant. In this way the diamine is deactivated and the stoichiometric balance is disturbed, resulting in a decreased molecular weight. To circumvent this problem a base should be added that is stronger than the diamine monomer. We have chosen triethylamine (TEA) to act as hydrogen chloride scavenger. For the synthesis of PPTA the addition of TEA is not necessary to obtain high molecular weight polymer since PDA is a weak base. However, the basicity of HDA is higher than PDA, and the use of an acid scavenger is essential to obtain high molecular weight PA 6,6. The next problem that occurs is that TEA is reactive with acid chloride end groups. Especially aliphatic acid chlorides are sensitive for side reactions and can react with TEA to form ketenes,[25] and both aliphatic and aromatic acid chlorides can react with TEA to form a monoamide group and an alkyl halide.[26] These side reactions are shown in Scheme 2. The reaction rate of these chain-terminating side reactions compared to the amide-forming condensation reaction can be suppressed significantly by decreasing the temperature. Temperatures in the range of −40 to 0 °C are desirable, and therefore the polymerization reactor was kept in an ice bath during the synthesis. Because of the reactivity of the TEA toward acid chloride, we have chosen to synthesize the block copolymer from an amine-terminated PPTA-oligomer; i.e., we use an excess of PDA in the oligomer synthesis.

Because of the complications mentioned above the final molecular weight of the PPTA-*b*-PA block copolymer will be lower than obtained for pure PPTA. Because aliphatic acid chloride is more sensitive to side reactions than aromatic acid chlorides, the molecular weight of the final copolymer in general will decrease with increasing PA content (see Table 3).

Extraction and ^{1}H NMR Analyses of PPTA-PA 6,6 Block Copolymers. All copolymer samples were extracted with formic acid, which is a solvent for PA 6,6 but a nonsolvent for PPTA by a Soxhlet extraction procedure. The results of the extraction procedure are shown in Table 2. The absence of any components in the precipitate of copolymer samples **P10-4**, **P4-4**, and **P10-10** along with the increase of the inherent viscosity of the copolymers compared to the oligomers (as shown in Table 1) are good indications that the PA is indeed copolymerized with the PPTA. However, a substantial part of the **P4-10** sample could be extracted by formic acid. This does not necessarily mean that the entire extracted fraction was not copolymerized (i.e., is pure PA). The ^{1}H NMR spectrum of the extracted fraction of **P4-10** shows the presence of PPTA in the extracted fraction. This indicates that the PPTA in the extracted fraction must be copolymerized with the PA because pure PPTA even with low degree of polymerization is insoluble in formic acid. Therefore, these results indicate that copolymer chains with low PPTA content (up to ∼15 wt %) are soluble in formic acid. Also, the molecular weight of the extracted part of polymer **P4-10** is significantly lower than of **P4-10** because the absorption peaks in the ^{1}H NMR spectrum are sharper.

^{1}H NMR measurements in D_2SO_4 were done for all copolymer samples, and the spectrum and peak assignment for polymer **P10-10** are shown in Figure 2.

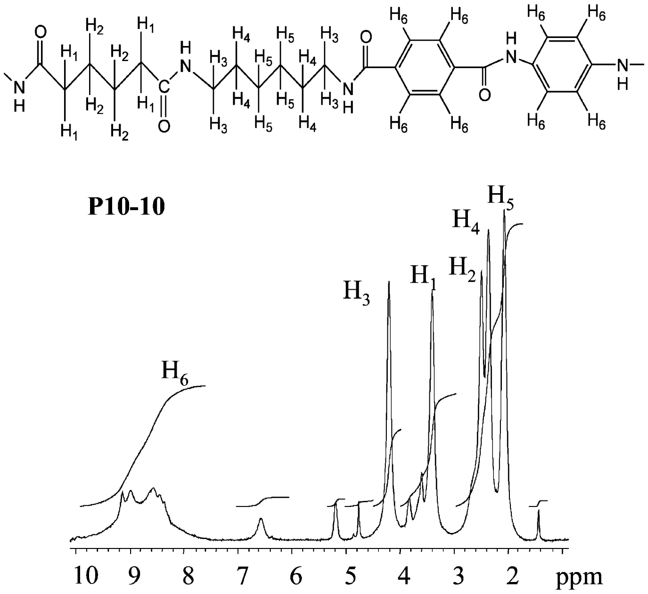


Figure 2. ^{1}H NMR spectra copolymer **P10-10**.

The area underneath the peaks from the protons in the PPTA (δ range 7.0−9.0 ppm) was compared to area from the absorption of the protons in the PA 6,6 (δ range 1.0−5.0 ppm). From the ratio of the two areas the copolymer composition is determined. The amide protons of both PPTA and PA 6,6 are capable of exchanging with the deuterium of D_2SO_4 and will therefore be part of the intense sulfuric acid signal observed around 12 ppm. The weight fraction of flexible polyamide calculated from the NMR spectra is compared with the fraction calculated from the theoretical composition, and the results are shown in Table 2.

According to Table 2, the $\varphi_{PA6,6}$ for all copolymer samples calculated from NMR analysis is significantly higher than the predicted weight fraction according to the theoretical composition. This overestimation of the weight fraction of the aliphatic part can be attributed to the process that besides the amide protons also the aromatic protons are capable of deuterium exchange in concentrated D_2SO_4.[27,28] Tam-Chang[28] observed that this deuterium exchange process increases with increasing temperature but already to some extent takes place at room temperature. Because of this deuterium exchange process, a systematic error is made that results in an overestimation of $\varphi_{PA\ 6,6}$ in the range of 5−10% for all our copolymers.

Molecular Mass Determination. Viscosimetry. Viscosimetry in concentrated (96 wt %) sulfuric acid was performed in order to determine the intrinsic viscosities $[\eta]$ of the block copolymers. The intrinsic viscosities were calculated by extrapolating the reduced viscosities to zero concentration. For all copolymers the reduced viscosity was linearly dependent on c for $0.2 \leq c \leq 0.5$ g/dL, which means there was no observable "polyelectrolyte effect" for this concentration range. This behavior is in accordance with the results reported by Schaefgen et al.,[29] who observed for pure PPTA that the positive charges generated by protonation along the polymer backbone are shielded due to the high concentration of counterions in 96% H_2SO_4, therefore allowing the polymer molecules to take a natural conformation over this concentration range. The intrinsic viscosity relates to the viscosity average molecular weight M_v according to the well-known Mark−Houwink equation:

$$[\eta] = KM_v^{\ a} \tag{1}$$

where K and a are constants for a given system. Determination of molecular weights of the type of block copolymers considered here is somewhat troublesome because no values for the parameters K and a are available. In fact, dilute solution behavior of block copolymers in general remains an area of controversy, and particularly for block copolymers comprised of rigid and flexible segments only few theories are available.

The intrinsic viscosity of a block copolymer material $[\eta]_{block}$ in a nonselective solvent can be estimated by a simple linear average of the corresponding intrinsic viscosities of the homopolymers if the polymer chain is considered as an idealized random-flight model with no mutual interactions.[30] For a binary block copolymer this results in

$$[\eta]_{block} = \phi_1[\eta]_1 + \phi_2[\eta]_2 \tag{2}$$

where φ_1 and φ_2 represent the weight fraction and $[\eta]_1$ and $[\eta]_2$ the intrinsic viscosities of the individual components. Of course, if polymers are comprised of rigid segments, the use of random flight statistics is far from plausible, and a simple linear relationship of the intrinsic viscosities will not suffice. A useful model that describes the intrinsic viscosity behavior of rod−coil diblock copolymers has been developed recently by Cavalleri et al.[31] Although, since we are dealing with multiblock copolymers, this model is not fully applicable for our polymers. We therefore have modified this approach in order to describe the intrinsic viscosity behavior of a rod−coil multiblock copolymer. Here, an alternating rod−coil copolymer is assumed of which the chains are composed of a sequence of rigid rodlike blocks **A** of length L and flexible coil blocks **B** that are described as a freely jointed chain of n segments with length l. The unperturbed mean-square end-to-end distance $\langle R^2\rangle$ of the individual blocks is

$$\langle R^2\rangle_A = L^2 \quad \text{for the rigid blocks} \tag{3}$$

$$\langle R^2\rangle_B = nl^2 \quad \text{for the flexible blocks} \tag{4}$$

To calculate the unperturbed mean-square end-to-end distance of the block copolymer, we need to take the average of the squares because we do a summation of statistically independent (Gaussian) events. The $\langle R^2\rangle$ of a rod−coil block copolymer consisting of N repeating units can be given by

$$\langle R^2\rangle = N(L^2 + nl^2) \tag{5}$$

The intrinsic viscosity $[\eta]$ in general is proportional to the ratio of the hydrodynamic volume V_h of the polymer to its molar mass M:

$$[\eta] = 2.5N_{AV}\frac{V_h}{M} = 2.5N_{AV}\frac{\langle R^3\rangle}{M} \tag{6}$$

where N_{AV} is the Avogadro number. The molar mass of the block copolymer $M_{copolymer}$ can be written as

$$M_{v,copolymer} = NM_{AB} \tag{7}$$

where M_{AB} is the mass of the repeating unit in the block copolymer. By substituting eqs 5 and 7 into eq 6, the intrinsic viscosity of the rod−coil block copolymer $[\eta]_{copolymer}$ can be written as

$$[\eta]_{copolymer} = 2.5N_{AV}\frac{(N(L^2 + nl^2))^{3/2}}{NM_{AB}} = \frac{2.5N_{AV}}{M_{AB}}(L^2 + nl^2)^{3/2}N^{1/2} \tag{8}$$

Analogous equations can be written for the individual blocks

$$M_A[\eta]_A = 2.5N_{AV}(L^2)^{3/2} \tag{9}$$

$$M_B[\eta]_B = 2.5N_{AV}(nl^2)^{3/2} \tag{10}$$

where M_A and M_B represent the molar masses and $[\eta]_A$ and $[\eta]_B$ the corresponding intrinsic viscosities of respectively the A and B blocks. If we substitute eqs 9 and 10 into eq 8, we obtain

$$M_{AB}[\eta]_{copolymer} = N^{1/2}((M_A[\eta]_A)^{2/3} + (M_B[\eta]_B)^{2/3})^{3/2} \tag{11}$$

and because $N = M_{v,copolymer}/M_{AB}$, we finally get

$$M_{AB}^{\ 3/2}[\eta]_{copolymer} = M_{v,copolymer}^{\ \ 1/2}((M_A[\eta]_A)^{2/3} + (M_B[\eta]_B)^{2/3})^{3/2} \tag{12}$$

According to this result, the intrinsic viscosity of the rod−coil block copolymer scales with the molecular weight to the power 0.5. This is analogous to a polymer that obeys random chain statistics dissolved in a Θ solvent. In reality, however, this is not true, nonideal behavior of the individual blocks in a good solvent, and the rigidity of the aramid blocks will cause that parameter a will be higher than 0.5. It is more plausible that parameter a for the block copolymer is between the values of the individual homopolymers. Values for parameter a of PA

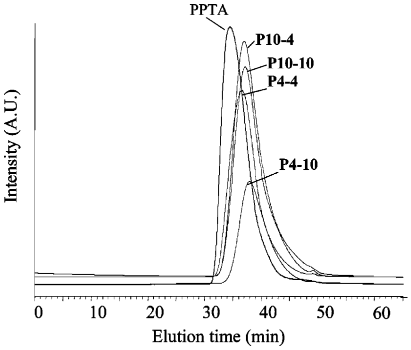


Figure 3. SEC elution curves for PPTA 1010 reference yarn (MW ≅ 32 000) and for the copolymers.

6,6 and PPTA in concentrated sulfuric acid are respectively 0.69[32] and 1.09.[33] Therefore, we rewrite eq 12 and define an α-parameter which is between 0.69 and 1.09, which replaces the scaling factor of 0.5.

$$M_{\mathrm{AB}}^{1+\alpha}[\eta]_{\mathrm{copolymer}} = M_{\mathrm{v,copolymer}}^{\alpha}((M_{\mathrm{A}}[\eta]_{\mathrm{A}})^{2/3} + (M_{\mathrm{B}}[\eta]_{\mathrm{B}})^{2/3})^{3/2} \quad (13)$$

Using this semiempirical approach, the molecular weight range for the block copolymer can be estimated. The molecular weight ranges of our copolymer samples calculated with eq 13 are shown in Table 3; the values of the intrinsic viscosities of the individual blocks needed for the calculations are given in Table 1. Results are compared with results obtained from SEC analysis treated in the next section.

SEC Analysis. Results obtained by SEC analyses, i.e., values for M_n, M_w, and the polydisperisty index (PDI), are also displayed in Table 3. The applicability of SEC for measurements of molecular weights of aramid type polymers is limited because only few solvents for aramids are known, and most of them are harmful for columns and filters of the SEC apparatus. Another limitation of the use of SEC is that absolute values of molecular weights cannot be obtained because no aramid fractions with well-defined molecular weight are available for calibration. The apparatus used was calibrated with polystyrene standards in THF. In addition, the polymers concerned here are not aramids but block copolymers containing aramid segments; therefore, the results obtained for SEC analyses should be regarded as a rough estimation for the molecular weights. However, results obtained from SEC do give an indication of the molecular weight distribution. The SEC elution curves of the block copolymer samples and the PPTA homopolymer reference are shown in Figure 3.

Next we will compare results of the molecular weights calculated from intrinsic viscosities (M_v) with the results obtained by SEC (M_n and M_w). In general, M_v is between M_n and M_w and tends to be close to M_w for rigid polymers and polymers with a broad molecular weight distribution, i.e., high index of polydisperisty. Since both factors are valid here, it is plausible to state that M_v should be close to M_w. From our results it is clear that that $M_v > M_n$ for all copolymer samples, and we find M_w values to be in the same range as the M_v values obtained via viscosimetry using eq 13. This indicates that by combination of the results of both methods we obtain a reasonable approximation for the molecular weights of this type of aramid−amide block copolymers. Nevertheless, it is clear that the determination of molecular mass of rod−coil block copolymers is not straightforward. The present approach gives consistent results between the various methods, but it should be noted that eq 13 is only a rough estimate. So far we have not succeeded in finding a more rigorous derivation for the [η] of a rod−coil block copolymer. This is due to the fact that both block are nonideal and have different Mark−Houwink exponents *a*.

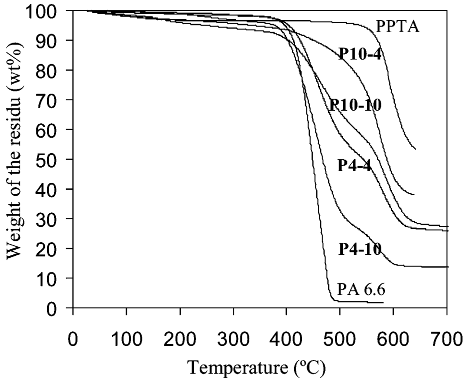


Figure 4. TGA of PPTA (MW ≅ 32 000), PA 6,6 (MW ≅ 16 000), and the copolymers.

TGA. TGA measurements in nitrogen have been performed to determine the thermal stability of the block copolymer samples. Pure PPTA and PA 6,6 samples with M_w around 30 000 were used as a reference. From the curvature of a TGA plot it is possible to distinguish between random and block copolymers because with increasing block length a block copolymer tends to behave more like a blend of the homopolymers. A block copolymer should therefore show two distinct degradation zones, while for a random copolymer a more gradual degradation is expected. Our results of the TGA measurements are shown in Figure 4.

From this figure it is clear that the stability of the polymers increases with increasing amount of PPTA. However, copolymer sample **P10-10** shows a somewhat higher thermal stability than sample **P4-4**, which might be attributed to the higher fraction of PPTA in this copolymer which is also observed from the NMR spectra. Block copolymer samples **P4-4**, **P10-10**, and **P4-10** show two distinct reductions in mass at 400 °C due to degradation of the PA 6,6 blocks and at 550 °C due to degradation on the PPTA blocks. Copolymer **P10-4** with highest amount of PPTA does not show a distinct degradation of the PA blocks but shows a more gradual reduction in mass. The degradation of PA 6,6 in this sample is therefore somewhat protected by the PPTA, which can be an indication that the PA 6,6 is more or less randomly distributed in the PPTA.

Conclusions

Four rod−coil block copolymers that are composed of alternating flexible PA 6,6 and rigid PPTA blocks differing in block length have been synthesized by a low-temperature polycondensation method. Molecular weights of the copolymers are lower than for PPTA obtained by the same synthetic procedure because of some side reactions in the PA 6,6 synthesis. However, the molecular weights of copolymers with an aramid content of at least 50% are sufficiently high for preparing films and fibers. By means of a combination of the characterization methods, notably Soxhlet extraction, NMR, and TGA as well as the observation that the intrinsic viscosity of the block copolymers increases substantially compared to the corresponding PPTA oligomers, it has been proven that a block copolymer is obtained. Because the block copolymers have been synthesized via a condensation method, a broad distribution in molecular weight is obtained which is confirmed by SEC analysis. A semiempirical model is described that relates the intrinsic viscosity of a rod−coil multiblock copolymer to its molecular weight, which in combination with SEC analysis appears to give a good approximation of the molecular mass of this type of alternating aramid−amide block copolymers.

Concentrated solutions of this type of block copolymers are likely to form a lyotropic liquid crystalline phase in sulfuric acid if the fraction of PPTA and the length of the PPTA blocks in the copolymer are sufficient. The phase behavior in sulfuric acid as well as a structural investigation in the solid state and the determination of the mechanical properties of the block copolymers will be dealt with in following papers.

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Supporting Information Available: ^{1}H NMR spectra of all prepared copolymers: **P10-4**, **P10-10**, **P4-4**, **P4-10**, and **P4-10** extracted; see Figure 2 for assignment of the peaks. This material is available free of charge via the Internet at http://pubs.acs.org.

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