A Study on the N-Allylation Reaction of Aromatic Polyamides. 1. Poly(*p*-phenylene terephthalamide)

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Received December 27, 1999

ABSTRACT: Aromatic polyamides represent an important class of polymeric materials from both the academic and the industrial points of view. Unfortunately, because of strong intermolecular interactions mainly due to hydrogen bonding, their solubility in common organic solvents is often extremely poor. In most cases, this drawback does not allow aramide molecular characterization. In the present work, the above difficulties have been overcome by a functionalization reaction leading to *N*-allyl derivatives of the parent aramide, that are easily soluble in organic solvents. Poly(*p*-phenylene terephthalamide) has been chosen as the reference aramide to be functionalized, on the basis of its industrial relevance as well as its insolubility in all organic media. Molar mass distribution of its N-allylated derivative has been obtained by SEC, using chloroform + 0.3% acetic acid as mobile phase, thus allowing full molecular characterization of the parent polymer.

Introduction

Aromatic polyamides (aramids) form a relevant family of polymers that in the past decades have attracted great interest of many research groups, at both the academic and industrial levels, not only as high performance materials but also for their peculiar conformational and physicochemical behaviors. The presence of both aromatic and amide groups, differently linked and oriented along the chain, allows for the preparation of a wide variety of aramide structures, ranging from flexible to rigid ones. For instance, *meta* structures provide flexible aramids, whereas all-*para* substitution leads to rigid chains. As a consequence, thermal, mechanical, and solution properties considerably vary from a structure to another. As an example, poly(*m*-phenylene isophthalamide) (Nomex) is a flexible polymer with good solubility in dimethyl sulfoxide, *N*,*N*-dimethylacetamide, sulfuric acid, etc., while poly(*p*-phenylene terephthalamide) (PPDT) (Kevlar, Twaron) is a rigid polymer, only soluble in concentrated sulfuric acid.

In general, the chain rigidity of a macromolecule represents a valuable property, being the prerequisite necessary to develop liquid crystalline behavior in the melt and/or solution at suitable concentrations. Because all-*para* aramids are characterized by melting temperatures higher than their thermal decomposition ones, liquid crystalline mesophases of the above polymers can be obtained only in solution. Their processing from the partially ordered state (the lyotropic mesophase) leads to materials characterized by superior mechanical properties (high elastic modulus, high tenacity, etc.).

Full molecular characterization of the above polymers by evaluation of the entire distribution curve of their molecular weights (MW) would be very relevant in order to optimize potential applications in various fields, but is rather difficult to perform for the aforementioned reasons. Moreover, although traditional methods (i.e. light scattering, viscometry, etc.) may in principle be applied for measuring average MW values, for their utilization it is required that polymers could be dissolved at the molecular level in the chosen solvent medium. For the majority of aramids this is not the case, as relevant aggregation phenomena are present even at very low polymer concentration. As an example, poly(*p*-benzamide) (PBA) gives strong aggregates in aprotic solvents (such as *N*-methyl pyrrolidone or *N*,*N*-dimethylacetamide, both containing a few percent of LiCl), thus preventing its molecular characterization in the above solvents; only concentrated H_2SO_4 can provide true molecular solutions of PBA. These drawbacks are obviously amplified when one deals with the evaluation of the molecular weight distribution (MWD) curve. Even with H_2SO_4 severe problems exist; for instance, some degradation of the polymer cannot be prevented and should be accurately taken in account in order to avoid misinterpretations of the results.

In recent years it has been suggested[1−3] that N-allylation of aromatic amide groups strongly decreases the stiffness of the polyamide chain, increasing at the same time its solubility in common organic solvents, owing to its capability of destroying hydrogen bonding. However, the potential application of the above functionalization reaction to size exclusion chromatography (SEC) analysis has not been described in the literature yet, although, provided that no degradation occurs during the substitution reaction and the latter is fully reproducible, N-allylated samples could in principle be easily analyzed by conventional SEC. In the present

10.1021/ma9921605 CCC: $19.00

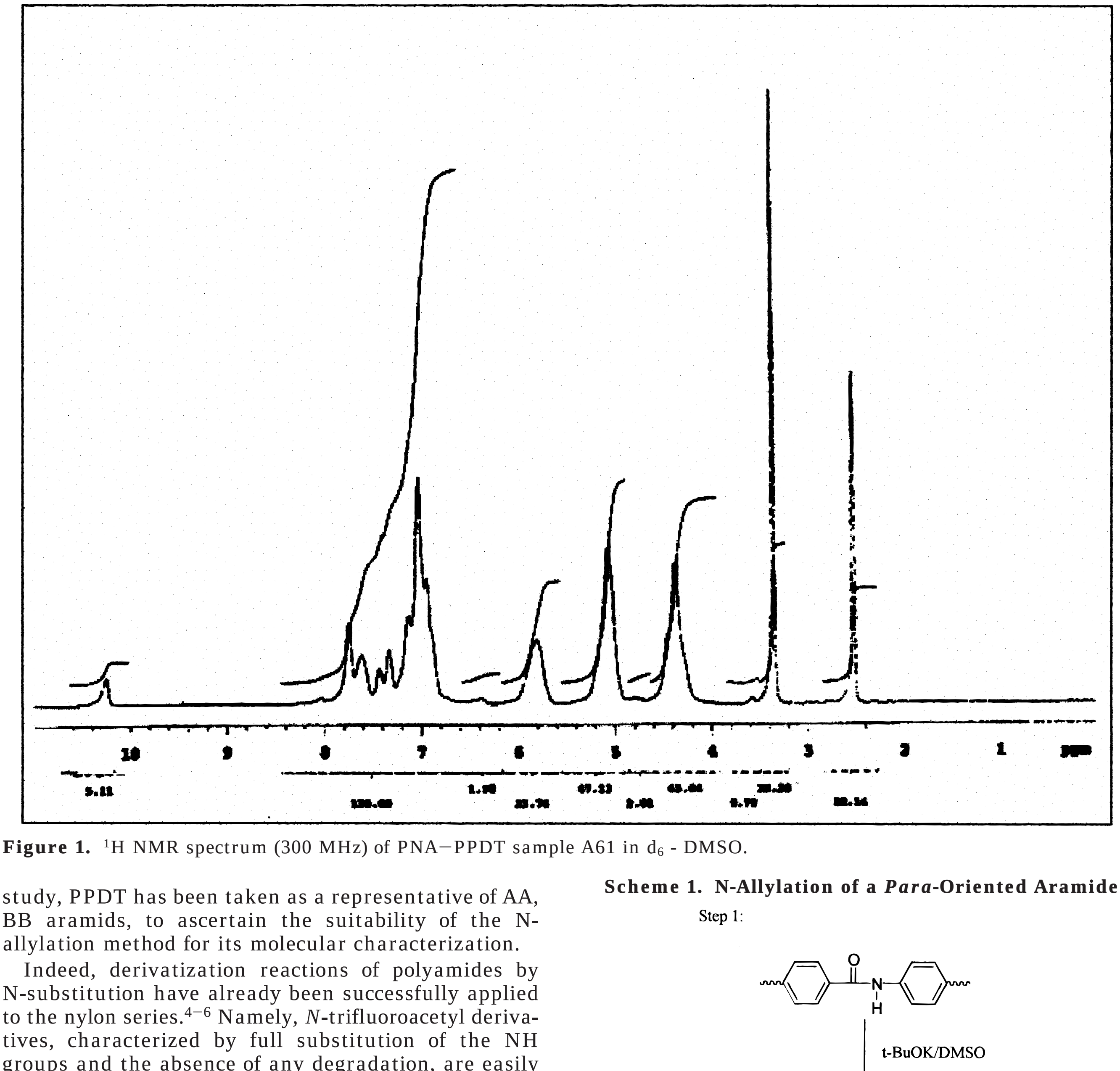
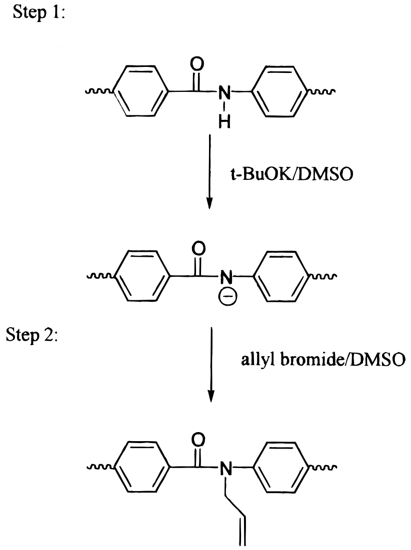


Figure 1. ^{1}H NMR spectrum (300 MHz) of PNA−PPDT sample A61 in d_6 - DMSO.

Scheme 1. N-Allylation of a *Para*-Oriented Aramide



study, PPDT has been taken as a representative of AA, BB aramids, to ascertain the suitability of the N-allylation method for its molecular characterization.

Indeed, derivatization reactions of polyamides by N-substitution have already been successfully applied to the nylon series.[4−6] Namely, *N*-trifluoroacetyl derivatives, characterized by full substitution of the NH groups and the absence of any degradation, are easily obtained from aliphatic polyamides. However, the above method completely fails when applied to aromatic polyamides.

Experimental Section

Materials. Commercial PPDT (Kevlar 49, DuPont) was finely cut and dried in a vacuum oven at 130 °C for 24 h before use. Laboratory samples of PPDT were synthesized according to a previous work of our research group[7] and treated as above. Potassium *tert*-butoxide (*t*-ButOK), allyl bromide, and anhydrous dimethyl sulfoxide (DMSO) (Aldrich) were used as received.

N-Allylation of PPDT. (i) Full substitution: in a three-necked flask, DMSO, PPDT (4.8%, w/v) and *t*-ButOK (2.47 mol per PPDT repeat unit) were introduced under nitrogen and kept stirred at room temperature for 48 h. During that time, because of the solubilization of PPDT polyanion in the initially heterogeneous reaction mixture, the medium became a red, viscous solution. After the first 24 h, the concentration of PPDT was lowered to 3.6% (w/v) by further addition of DMSO. After additional 24 h, allyl bromide was added (2.42 mol per PPDT repeat unit). Immediately, the solution became very fluid and, in about 3 h, *N*-allyl−PPDT (NA−PPDT) spontaneously precipitated. The derivatized polymer was recovered by filtration, washed with water and dried overnight in a vacuum oven at 70°C. (ii) Partial substitution: the only difference with the above procedure was the less than stoichiometric ratio of allyl bromide to PPDT amide protons in the repeat unit, as suggested in the literature.[2] As described in detail later on, partially substituted PPDT (PNA−PPDT) remains soluble in the reaction mixture.

Characterization. Solution viscosity measurements were performed by using a suspended level Ubbelhode viscometer

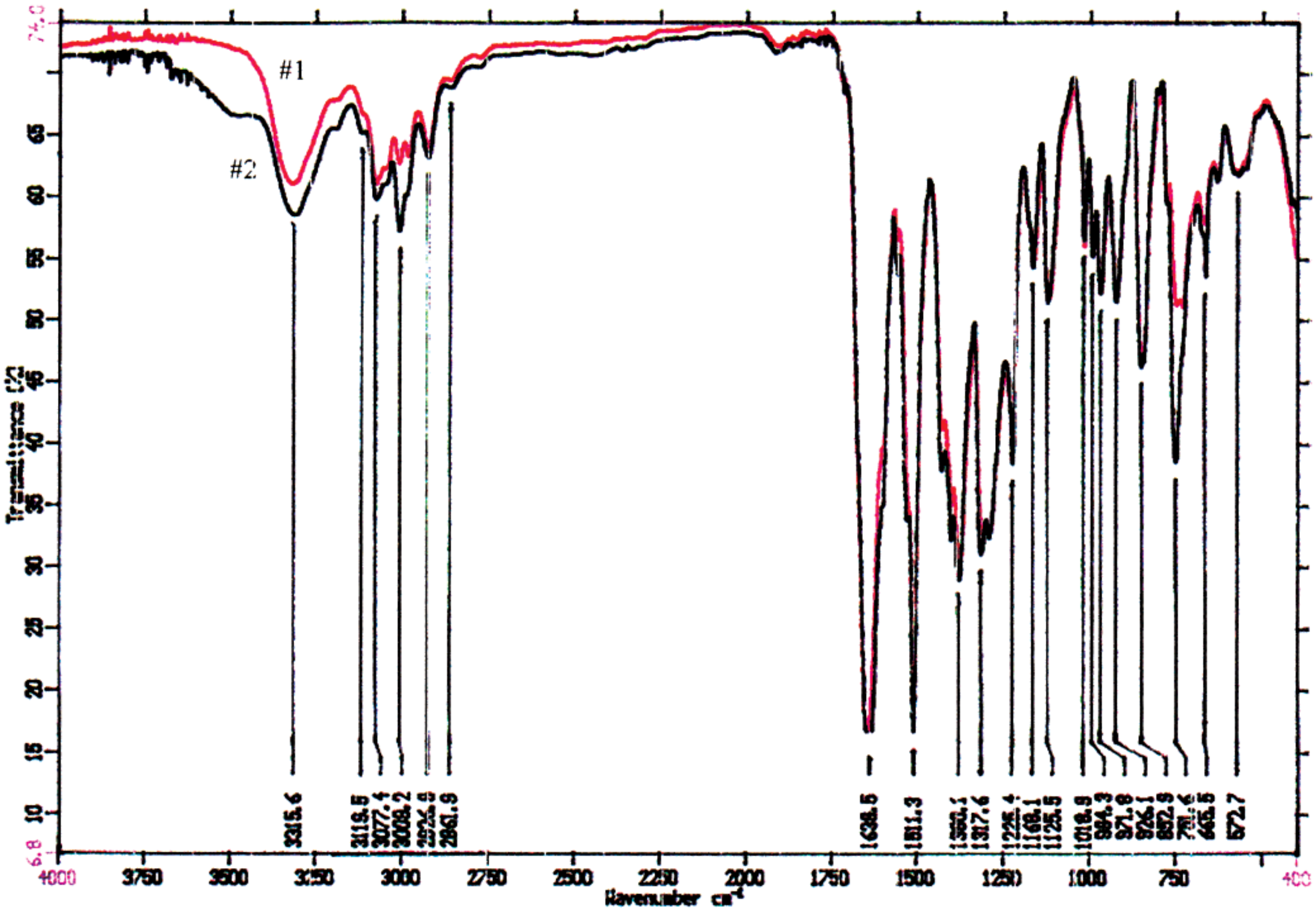


Figure 2. IR spectra of sample A61: (1) room temperature; (2) 110 °C.

Table 1. Intrinsic Viscosity Values of Some NA−PPDT Samples, As Compared to the Corresponding Values of Parent PPDT

sample	[η] of PPDT[a] (dL g^{-1})	[η] of NA−PPDT[b] (dL g^{-1})
A1[c]	8.05	0.43
A3[c]	8.05	0.37
A21[c]	1.84	0.16
A22[c]	1.84	0.14
A4[d]	5.80	0.31
A11[d]	5.80	0.29
A17[d]	5.80	0.32

[a] In 96% H_2SO_4 at 25 °C. [b] In $CHCl_3$ at 20 °C. [c] NA−PPDT from laboratory-made PPDT.[7] [d] NA−PPDT from Kevlar 49 commercial fibers.

under the following conditions: 96% H_2SO_4 at 25 °C, for PPDT; $CHCl_3$ at 20 °C, for *N*-allyl derivatives.

FTIR spectra were recorded by a Bruker IFS66 spectrophotometer on thin polymer films. To remove humidity from the samples, a SPECAC heating cell was used in the temperature range between 25 and 110 °C. ^{1}H and ^{13}C NMR spectra were performed in $CDCl_3$ or in d_6-DMSO by using a Gemini 200 or a Unity 300 Varian spectrometer. DSC analyses were carried out by a Mettler calorimeter mod. TC 10A (heating rate of 10 °C/min). TGA analyses were performed by a Perkin-Elmer thermal analyzer (Series 7) at a heating rate of 20 °C/min.

SEC Analysis. SEC characterization was carried out either by a conventional SEC apparatus or by a multidetector SEC system. Basically, in the conventional mode, the system consisted of an Alliance 2690 separation module and a differential refractometer (DRI) as the concentration detector (both from Waters, Milford, MA). In the above configuration the molar mass *M* was derived from polystyrene (PS) calibration, as usual. In the multidetector SEC system, two additional absolute detectors were used on-line: a laboratory-made single capillary viscometer (SCV) and a multiangle laser-light-scattering flow cell (MALS) (a Dawn DSP−F photometer from Wyatt, Santa Barbara, CA). Characteristics and performances of the multidetector SEC−MALS−SCV system have been described in detail elsewhere[8−12] and are summarized in refs 13−16.

The column set was based on two PLGel Mixed C columns (5 μm particle size) from Polymer Laboratories (Shropshire, U.K.). The experimental conditions used were as follows: chloroform + 0.3% acetic acid as mobile phase; temperature of 35 °C; flow rate of 0.6 mL/min and injection volume of 200 μL.

Results and Discussion

N-Allylation. As mentioned in the Introduction, to allow full molecular characterization of aramids, we decided to explore the possibility of synthesizing *N*-allyl derivatives of PPDT (as reference material), possibly fully functionalized, in reproducible conditions and without any degradation of PPDT chains.

At first, it has been necessary to verify whether the above derivatization occurs without any degradation of the aramid chain. Indeed, following Scheme 1, in the first step the strong base (*t*-BuOK) reacts with the −NH− amide groups to form a polyanion which, in the second step, is allowed to react with allyl bromide to give the final derivatized product. It is reasonable to assume that, as the base is a rather aggressive reagent, potential degradation could almost exclusively occur during the first step. To ascertain this point, some samples of PPDT have been treated with *t*-ButOK for 48 h as in Step 1 of Scheme 1, but instead of being further added with the N-allylating agent, they were

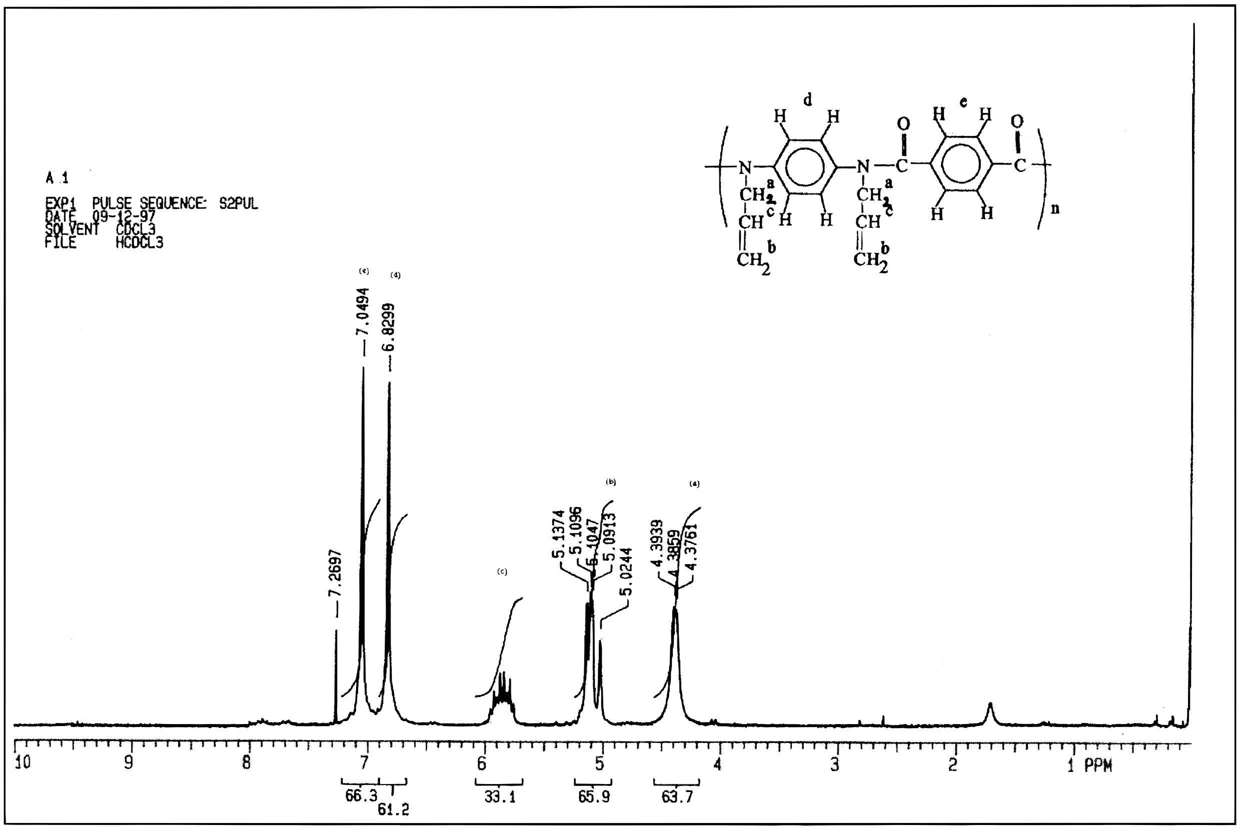


Figure 3. ^{1}H NMR spectrum (200 MHz) of NA−PPDT sample A1 in $CDCl_3$.

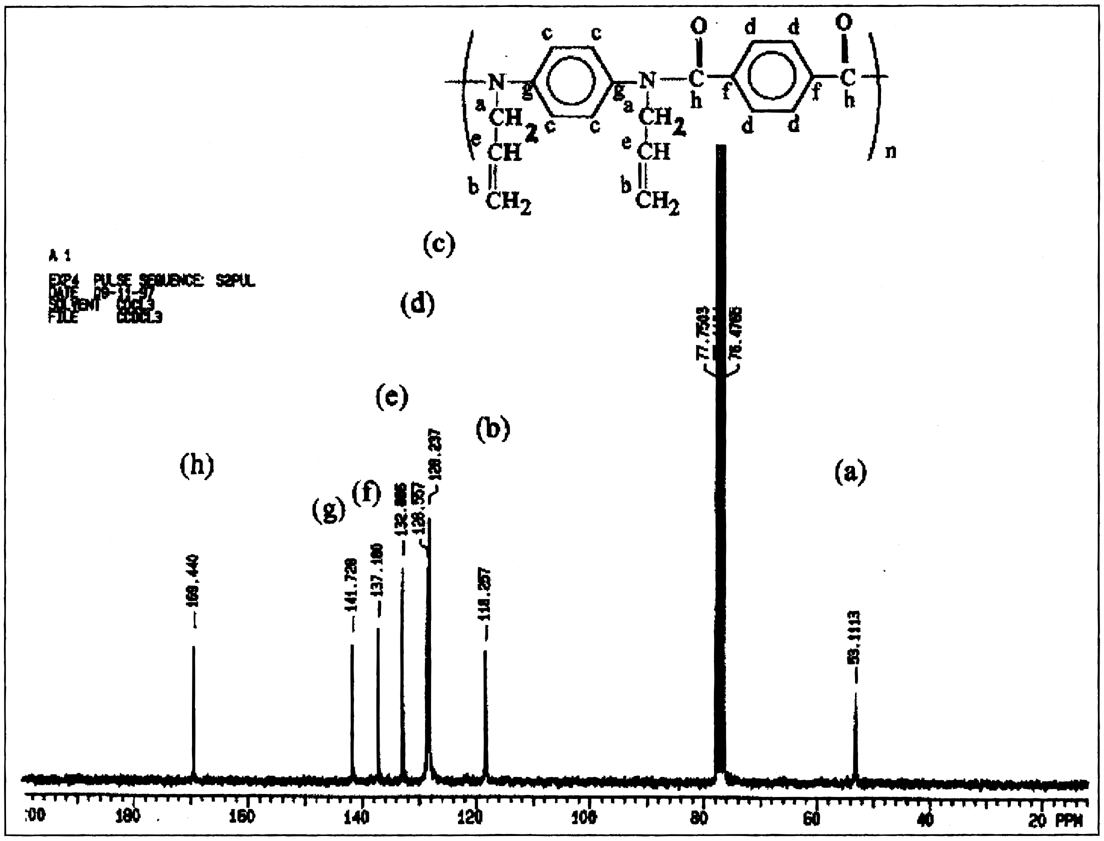


Figure 4. ^{13}C NMR spectrum (200 MHz) of sample A1 in $CDCl_3$.

quenched with water to give back the starting aramide. Intrinsic viscosities of treated samples in 96% H_2SO_4 have been measured and compared with those of neat PPDT. The [η] values for both series of samples have been found in all cases coincident (e.g., for sample A43, [η] = 2.55 dL g^{-1} before and after treatment). From the above data, it is reasonable to assume that no degradation occurs in our experimental conditions.

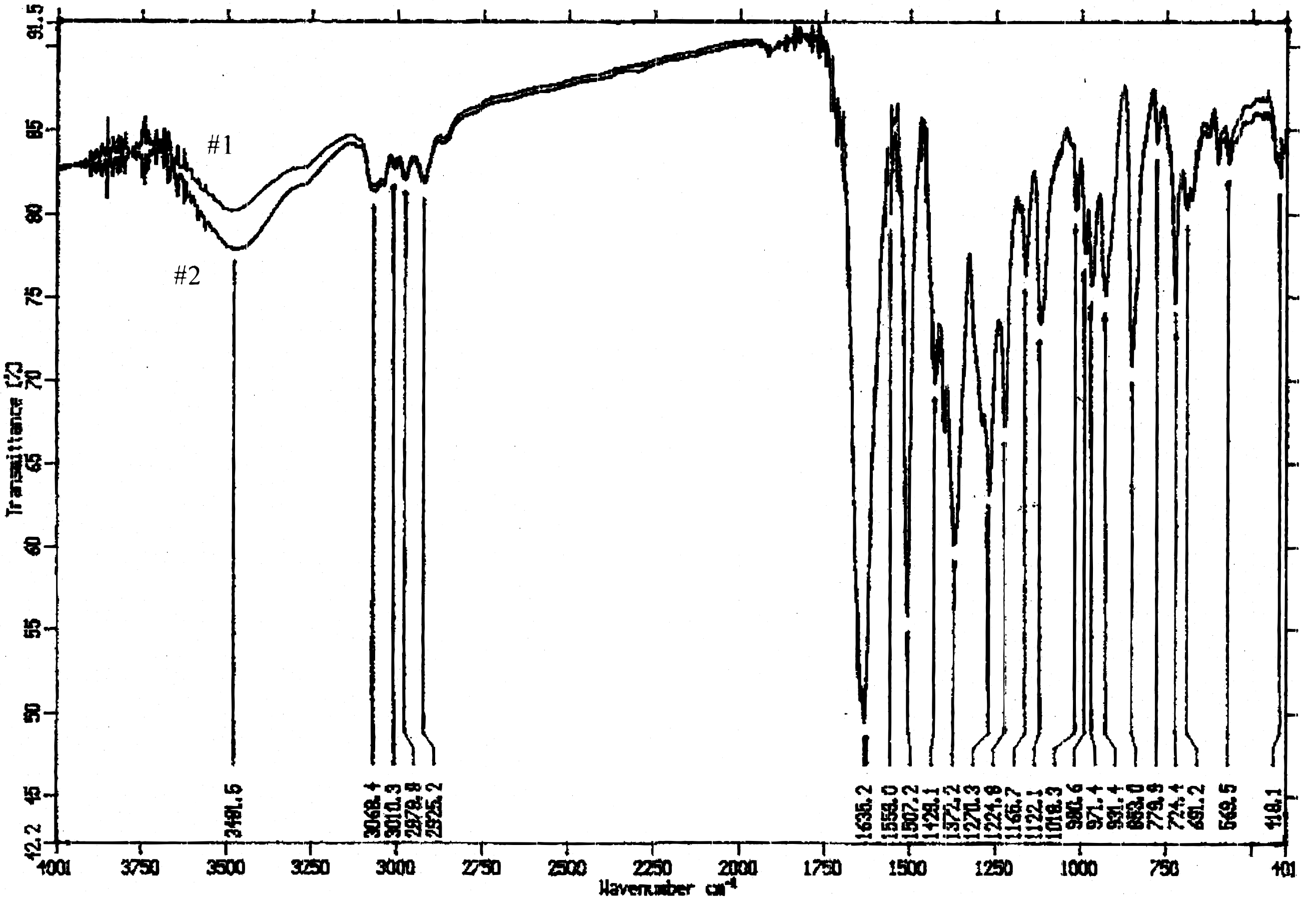


Figure 5. IR spectrum of NA−PPDT sample A14: (1) room temperature; (2) 110 °C.

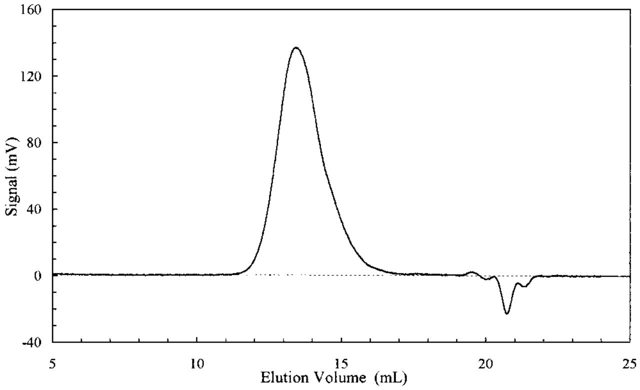


Figure 6. Chromatographic trace of the DRI detector for NA−PPDT sample A64.

Table 2. SEC Characterization Data of Four NA−PPDT Samples

	SEC[a]		SEC−MALS[b]		SEC−SCV[c]	
sample	M_w (g mol^{-1})	D	M_w (g mol^{-1})	D	[η] (dL g^{-1})	D
A36	20 420	2.9	31 800	1.6	0.187	3.0
A38	18 025	2.4	26 700	1.5	0.161	2.5
A63	36 100	2.4	42 600	1.5	0.244	2.6
A64	46 930	2.3	51 400	1.5	0.309	2.5

[a] Conventional SEC based on PS calibration. [b] On-line light-scattering detector. [c] On-line viscometry detector.

To check the other two points (full substitution and reproducibility) both partially and fully allylated PPDT samples have been prepared and characterized.

(1) Partially Allylated PPDT. These derivatives have been synthesized with the aim of comparing their structure, behavior, and properties with those of the corresponding fully allylated NA−PPDT samples. For the partial functionalization, degrees of allylation >75% have been chosen, as it is only beyond this degree of substitution that PNA−PPDT is soluble in common chlorinated solvents and in DMSO, thus making rather easy its molecular characterization. As mentioned in the Experimental Section, at variance with the full substitution runs where the N-allylated PPDT becomes insoluble in the reaction medium and gives a precipitate, the partially allylated product remains in solution throughout the reaction. Figure 1 gives the ^{1}H NMR spectrum (300 MHz) of a partially allylated PPDT sample (A61) in d_6-DMSO. The signals at 4−6 ppm clearly show the presence of the allyl group. A single peak, attributed to amide protons, is present at 10.2 ppm. The COSY ^{1}H−^{1}H analysis in DMSO confirms cross-peaks between the above signal and the aromatic protons at 7 and 7.7 ppm. The degree of substitution can easily be calculated from the ratio between the integrated area of amide protons and that of vinyl protons at 5.8 ppm. In the sample under consideration, that ratio has been found equal to ≈ 83%. The above value is in excellent agreement with that expected by the stoichiometric ratio between the amount of allylating agent used and that of amide protons (84%).

IR spectra of the same PNA−PPDT sample, taken at room temperature (spectrum 1) and 110 °C (spectrum 2), respectively, are reported in Figure 2. Signals at 3077, 3009, 2984, 2926, 2862, and 751 cm^{-1}, all linked to the allyl group, show shape and intensity variations as functions of T, as the allyl group is strongly affected by conformational changes induced by temperature rise.

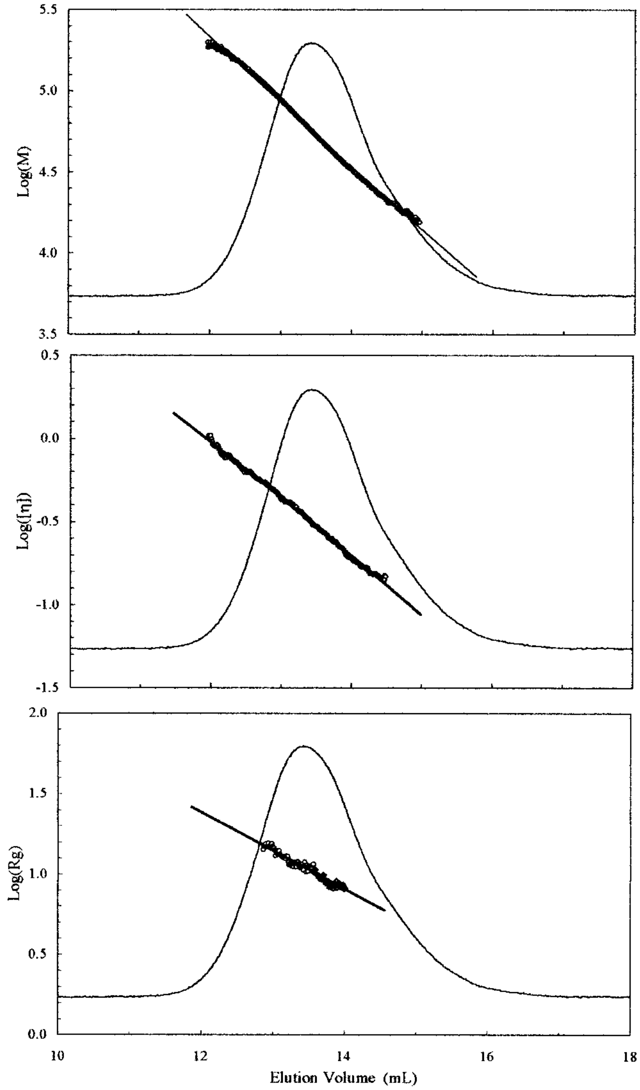


Figure 7. Experimental functions: M, $[\eta]$, and $R_g = f(V)$ from the data given by the SEC−MALS−SCV system (sample A64).

They are also present in the fully allylated samples (see later). In addition, a typical signal due to amide N−H stretching vibration (3315 cm^{-1}) is clearly visible already at room temperature. Support for the presence of unreacted amide protons is also provided by the shoulder of the band at 1511 cm^{-1}, due to secondary amides.

DSC analysis shows two different glass transitions, the first of which is at the same temperature of the fully allylated PPDT ($T_g \approx 150$ °C, see below), and the second one appears at higher temperatures ($T_g \approx 190-200$ °C). Therefore, it can be inferred that PNA−PPDT is formed by two kinds of amorphous domains, characterized by blocks having different degrees of allylation.

(2) Fully Allylated PPDT in H_2SO_4. Intrinsic viscosity data of some samples of both commercial and laboratory-made PPDT in H_2SO_4 are reported and compared with the corresponding values of their fully allylated derivatives in $CHCl_3$ (Table 1). It can be seen that, by starting from different batches of the same PPDT, the corresponding derivatives are characterized by rather close $[\eta]$ values, thus indicating excellent reproducibility of the N-allylation reaction. It should be pointed out that the strong tendency of $CHCl_3$ to evaporate made solution viscosity measurements difficult and exposed to relatively large fluctuations.

Disregarding relatively minor effects due to solvent change from sulfuric acid to chloroform, the more than 10-fold decrease of $[\eta]$ from neat PPDT to NA−PPDT underlines the transition from rigid to flexible chains. We will consider this aspect in detail further on.

Figure 3 shows the ^1H NMR spectrum of NA−PPDT (sample A1) in $CDCl_3$ (200 MHz). As already mentioned, signals in the range between 4 and 6 ppm are typical of allyl protons. Furthermore, the absence of peaks at 9−10 ppm (amide protons) suggests that full derivatization has been achieved. This is also confirmed by the ratio of the integrated areas of proper signals, (d + e)/(a + b + c) (see Figure 3 for attribution), found to be equal to 0.8, as expected for the full substitution.

Figure 4 gives the ^{13}C NMR spectrum of the same fully allylated PPDT in $CDCl_3$ (200 MHz), Again, peaks at about 120 ppm (attributed to carbons atoms linked to amide NH groups) are absent, as clear evidence of complete substitution.

A further confirmation that the N-allylation reaction has been quantitative is underlined by the IR spectrum given in Figure 5 for the sample A14. No traces of broad absorptions either at ca. 3300 cm^{-1} (amide NH) or at 1540 cm^{-1}, typical of secondary amides, are present. Instead, peculiar allyl group bands (at 910 and 980 cm^{-1}) and those of methylene groups (at 2920, 1460, and 725 cm^{-1}) are evident.

DSC analysis of an NA−PPDT sample (sample A30) shows a single glass transition at ≈150 °C, again supporting the structural homogeneity of its sequences along the chain. Second heating seems to induce some cross-linking through the allyl groups (at $T \approx 270$ °C), followed by complete degradation (at about 400 °C); thermal degradation is confirmed by TGA, which also shows a residue >20% in nitrogen atmosphere at 800 °C, due to incomplete combustion and high char formation, whereas no residue in oxygen has been found even at 600 °C.

On the basis of the whole set of the above results, we can therefore conclude that N-allylation of PPDT is reproducible, is quantitative, and occurs without any chain degradation.

SEC Characterization. As an example, Figure 6 shows the SEC trace of the A64 sample (DRI detector). Using PS calibration, relative molar mass data of four NA−PPDT samples are given in Table 2 (columns 2 and 3), as weight-average molar mass (M_w) and polydispersity index (D).

As mentioned above, a more precise molecular characterization of the NA−PPDT derivatives, in terms of absolute molar mass, intrinsic viscosity, and dimensions and conformation of the macromolecules, has been attempted by the multidetector SEC−MALS−SCV system. Figure 7 shows the experimental functions M, $[\eta]$, and $R_g = f(V)$, where V represent the elution volume, for the A64 sample. The broad range, in which M, $[\eta]$, and R_g of NA−PPDT are measured with acceptable accuracy, is clearly evident. A summary of the results obtained by the SEC−MALS−SCV system is also reported in Table 2. The discrepancy between the absolute M_w values, from MALS, and the equivalent PS values is relatively large. Moreover, this difference, approximately ranging from 9 to 35%, strongly depends on molar mass, being substantially higher for low molar mass samples. A comparison of the differential MWD curves (by SEC−MALS) for the four NA−PPDT samples is reported in Figure 8.

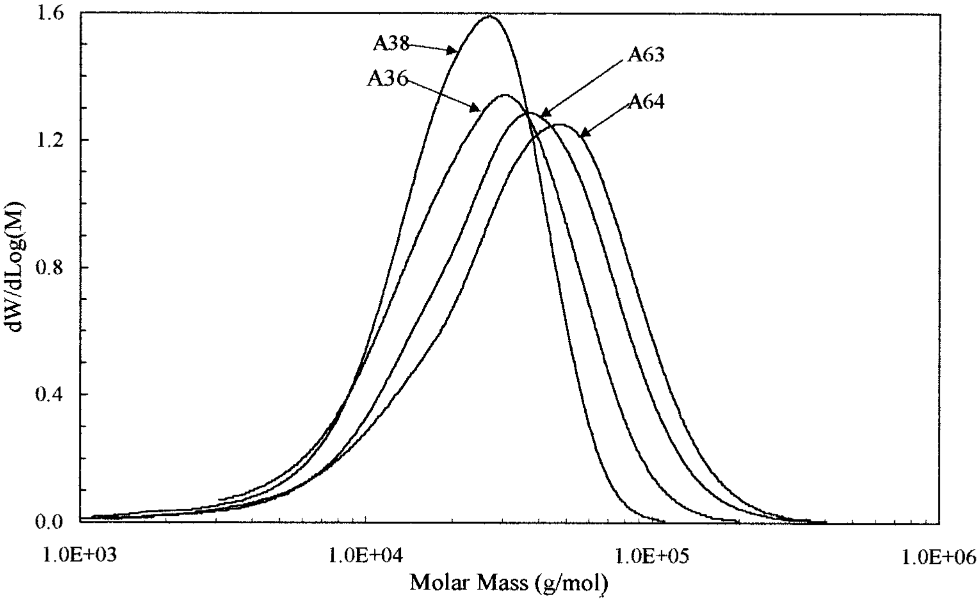


Figure 8. Differential MWD of four NA–PPDT samples.

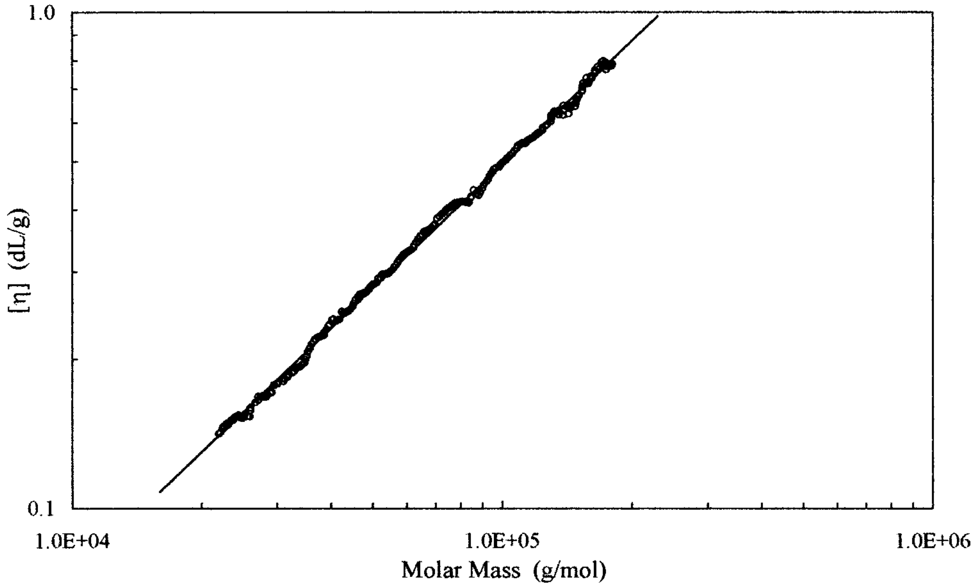


Figure 9. $[\eta] = f(M)$ power law (Mark–Houwink–Sakurada plot) for sample A64.

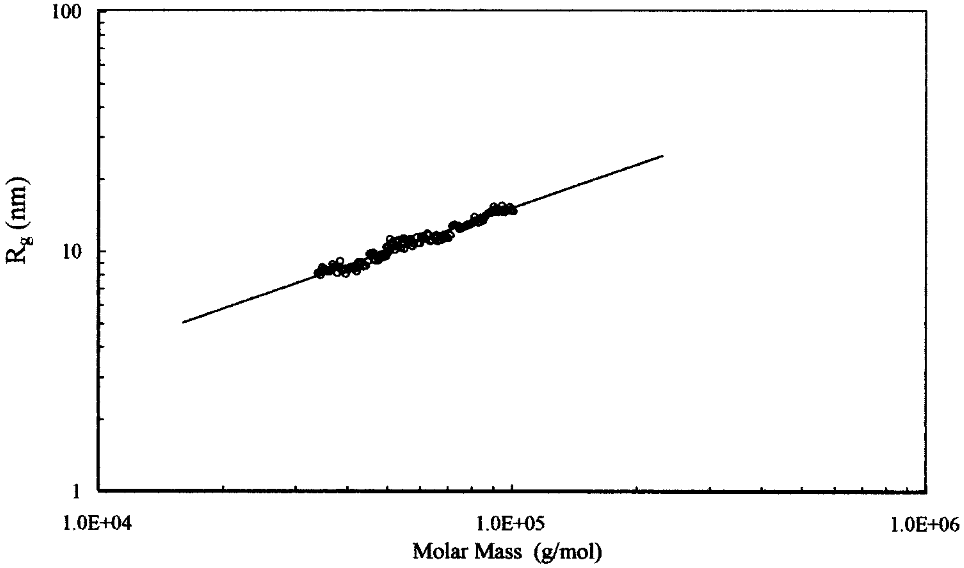


Figure 10. $R_g = f(M)$ power law for sample A64.

The polydispersity index *D* evaluated by SEC−MALS has been found substantially lower than the values obtained with the other two methods; however, the tendency of MALS detector to underestimate the *D* value is well-known, owing to its poor sensitivity to low molar mass fractions. Hence, the *D* values calculated by conventional SEC and SEC−SCV methods probably are a better evaluation of the actual values.

The intrinsic viscosity, evaluated by SCV data for the four NA−PPDT samples, is also given in Table 2 (penultimate column). $[\eta]$ values range from 0.16 to 0.31 dL/g. As compared to the data quoted in Table 1, differences between the two sets of $[\eta]$ values should be justified in terms of change of both the solvent medium and the temperature. The SCV data have been also used to estimate the coefficients of the $[\eta] = f(M)$ power law, i.e., the Mark−Houwink−Sakurada (M−H−S) equation. Figure 9 shows $[\eta] = f(M)$ for sample A64. The coefficients of the resultant M−H−S equation are as follows: $K = 3.99 \times 10^{-5}$, $a = 0.826$. It should be noted that the exponent $a = 0.826$ is typical of expanded polymer coils in a thermodynamically good solvent, whereas the value of 1.25 evaluated for neat PPDT[17] is characteristic of stiff chains.

A crude estimate of the *a* exponent of M−H−S equation for NA−PPDT can be evaluated also from the data of Table 1, i.e., from the $[\eta]$ values of PPDT and the corresponding NA−PPDT samples, together with their calculated M_w values.[17] The resultant *a* has been found equal to 0.82, in good agreement with the more accurate set of data from SCV. By multiplying the M_w values of NA−PPDT by 0.75 (ratio between the CRU equivalent weights of PPDT and NA−PPDT), data allowing full molecular characterization of poly(*p*-phenylene terephthalamide*)* are easily obtained.

Measurement of macromolecular dimensions by MALS requires that angular dependence of the scattering intensity be experimentally measurable.[18] Despite the narrow range in which R_g of our NA−PPDT samples has been appropriately measured, we tried to roughly estimate the slope of $R_g = f(M)$ power law using sample A64, characterized by the highest molar mass among the four samples (Figure 10). The slope of the straight line is approximately 0.61, again a typical value for expanded coils. It is obvious, in this case, that the accuracy of the evaluation is rather poor. However, all our results point to the same conclusion: NA−PPDT in the mobile phase takes a substantially flexible conformation. On these grounds, N-allylation is confirmed as a suitable method for destroying both hydrogen bonding and stiffness of aramid chains, making them prone to easy dissolution in common organic solvents.

Acknowledgment. Inspiring discussions with Dr. Y. H. Kim (DuPont) are gratefully acknowledged. The authors wish to thank Prof. Dusan Berek (Slovak Academy of Sciences, Bratislava), Dr. Giuseppina Conio (IMAG CNR, Genova, Italy), Sig. Alberto Giacometti Schieroni (ICM CNR, Milano, Italy), Dr. Emma Barchiesi (Ausimont CRS, Bollate, Italy) and Dr. Cinzia Tavani (DCCI, Genova, Italy) for their kind assistance in the present work. This research has been supported by "MURST-Cofinanziamento 1998" funds.

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(13) From the scattering intensity at zero angle the MALS detector provides molar mass, while from the angular variation it gives average dimensions of the macromolecule, i.e., the root-mean-square radius $\langle s^2\rangle^{1/2}$ (in the text denoted as radius of gyration, R_g). Furthermore, the on-line SCV detector provides the intrinsic viscosity, $[\eta]$. As a consequence, at each elution volume after fractionation by SEC columns, the multidetector SEC− MALS−SCV system gives M_i, R_{gi}, and $[\eta]_i$ for each NA−PPDT fraction.
(14) The calibration constant of the MALS detector has been calculated using toluene as standard, assuming a Rayleigh factor of 1.406×10^{-5} cm^{-1}. The photodiode angular normalization has been performed by measuring the scattering intensity of a very narrow, low molar mass PS standard ($M = 10.9$ kg/mol, $D < 1.03$, $R_g = 2.6$ nm), assumed to behave as an isotropic scatterer in the mobile phase.
(15) The differential refractive index increment, d*n*/d*c*, of the polymer with respect to the mobile phase at 25 °C has been measured by a Chromatix KMX-differential refractometer (LDC Milton Roy, Riviera Beach, FL). The d*n*/d*c* value of NA−PPDT is 0.170 mL/g.
(16) Addition of acetic acid to the mobile phase allowed to us overcome polymer adsorption problems and back-pressure increase, present when neat chloroform was used.
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(18) It is well-known that the minimum measurable R_g with a He−Ne laser (632.8 nm wavelength) is approximately 8−10 nm.

MA9921605