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CONDENSATION POLYMERS WITH CONTROLLED STRUCTURE(U)
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TECHNICAL REPORT

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CONDENSATION POLYMERS WITH CONTROLLED STRUCTURE

by

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1. Introduction

Wholly aromatic amides (aramides) represent a class of polymers of exceptional technological importance. Fibers with high mechanical strength and thermal resistance, obtained from nematic solutions of these polymers, are at present employed in a variety of industrial applications requiring extraordinary performances (1).

As stated in our last report, this project's objective is to investigate the effects of constitutional isomerism in aramides arising when non-symmetric substituents are introduced into the main chain. We initially conjectured that this isomerism should lead to profound changes in some (undesirable) macroscopic properties of the polymers while leaving others (desirable) unaffected. Our initial assumptions have so far been fully confirmed by our experiments. Constitutionally ordered polymers exhibited substantially higher relative solubilities compared to their more random counterparts. This effect could be observed for three different types of ring-substituents with varying electronic and steric properties and was independent of the solvent used. This behavior can be easily understood by correlating the ease of formation of crystal domains with structural order. The constitutionally regular aramides can easily form closely packed arrays with many hydrogen bonds between the chains. In the less ordered polymers on the other hand, the substituents, which are randomly positioned along the chain, sterically prevent formation of classical, crystalline domains with strong cohesive intermolecular forces. Differences in the percentage amount of water the polymers absorb can also be rationalized similarly. We observed that polymers with higher degree of constitutional regularity absorb substantially less moisture (up to 2.5% w/w) than the random ones (up to 4% w/w). The degree of water absorption of polymers has been previously correlated to their degree of crystallinity [2]. Other experiments confirmed on the other hand that the polymers retain their ability to form liquid crystalline phases, independently of their constitutional order. This ability is together with their rigid-rod character (for which we have further experimental evidence) is presumably the main causes for their advantageous properties.

In order to reliably correlate the polymers' macroscopic properties to their constitutional order it is of paramount importance to examine well-defined and well-characterized systems. We dedicated a great effort to this aspect of our work. We tried to solve the problem of determination of the polymers' structural regularity in two independent ways. On one hand, we calculated expected values for the order parameter s for all the compounds we synthesized applying the theory constitutional isomerism (3). In the beginning, we mainly used approximate values from literature [4] for the relevant kinetic parameters k_a , g_a , g_b and r for. During last year, we experimentally determined values (or approximations) for these parameters ourselves. This has greatly increased the accuracy of our computer models. On the other hand

nuclear magnetic resonance (NMR) ←

↑
we tried to determine the structural order of our polymers directly through NMR. Here, we also greatly improved our capabilities during last year. We are now able to quantitatively determine the order parameter for our polymers with inherent viscosities up to $\eta_{inh} = 1.3 \text{ dl/g}$. NMR peaks of higher molecular weight polymers are too broad to be resolved, so that no information about s is obtainable in these cases.

We also succeeded to determine values of M_n using vapor pressure osmometry (VPO). This has not been a trivial endeavour (due to the unusual solvents that need to be used), and to our knowledge this is the first time VPO measurements have been performed on aramides. This allows us to determine values for the Mark-Houwink constants K and a which give us further information about the conformational properties of our systems. We finally ran various size exclusion chromatography (SEC) experiments which gave us information about the molecular weight distribution (M_w/M_n ratio) of the polymers.

We have synthesized various modified aramides from three different substituted non-symmetric monomers covering the range of s values from $1/2$ to nearly 0 (which corresponds to random polymers and ordered head/head, tail/tail, respectively). We have been able to determine s directly and quantitatively in many cases, and we have finally investigated some relevant properties of these systems.

2. Polymers Synthesized

2.1. General

We synthesized three different types of aramids using non-symmetrically substituted monomers with high differences in their reactivity ratios (having low values of r).

The compounds synthesized are:

poly(2,6-dichloro-p-phenylene terephthalamide) (I)

poly(2-nitro-p-phenylene terephthalamide) (II)

poly(2-methoxy-p-phenylene terephthalamide) (III).

Whereas in the previous funding period of this project only polymer (I) could be synthesized in both, ordered and random forms, all three compounds could be obtained with different degrees of ordering (with values for s ranging from almost 0 to 1/2) during the last year. Order was controlled by variation of the monomer feed rates and could be verified in many cases quantitatively using ^1H nmr.

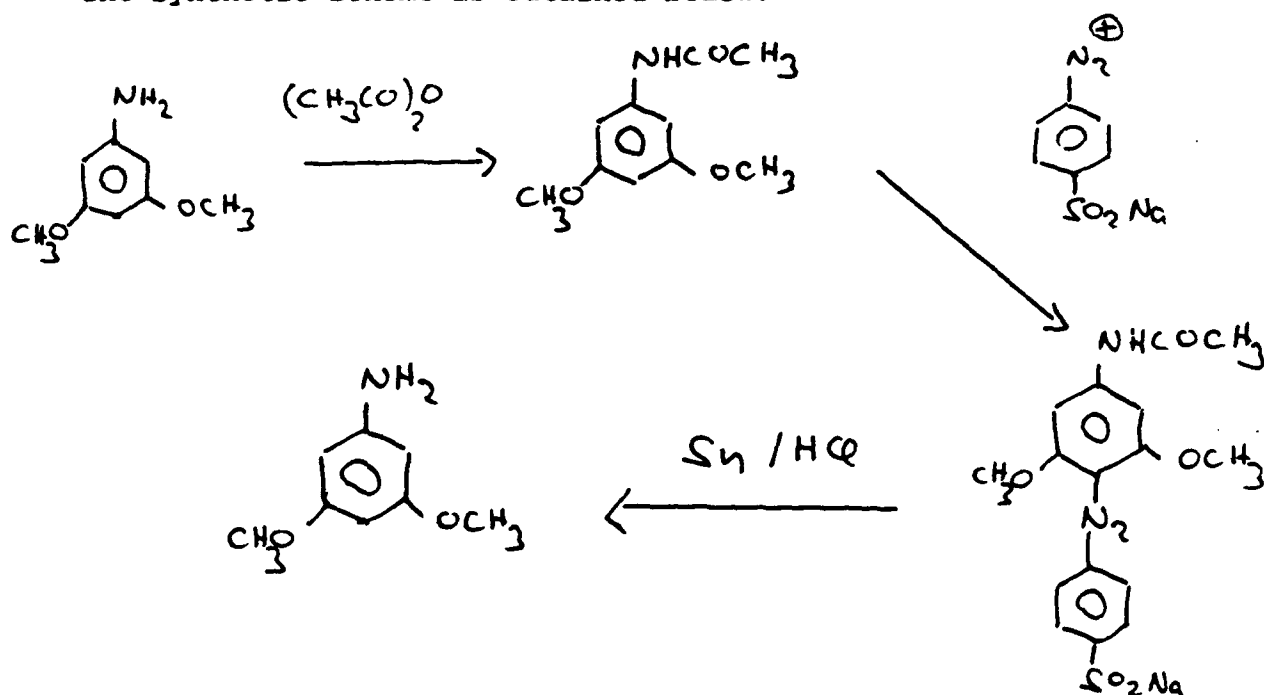
2.2. Synthetic Techniques

The synthetic techniques developed during the second funding period was very successful and was maintained. A small modification of the solvent used (we changed from N-methylpyrrolidone to N-ethylpyrrolidone) resulted in slightly better molecular weights obtained. This can probably be explained by the lower reactivity of this solvent towards terephthaloyl chloride, which minimizes even further the side-reaction.

Further improvement in the work-up of the polymers was made. The importance of washing and heat treatment of the compounds after synthesis in order to obtain well-characterized material was realized. Elemental analyses of the raw material showed that considerable amounts of decomposed solvent and other impurities are normally trapped into the precipitated material. Thorough washing with water at about 70°C, followed by washing with acetone at room temperature drastically improved the results of our elemental analyses determinations. Heat treatment of our samples dramatically improved the reproducibility of our moisture absorption experiments. This is consistent with other observations made elsewhere [2] and can be explained by the fact the polymers cannot attain their optimal solid state "conformation" in the very short time they are precipitated from solution.

3. Monomer Preparation

As we have noted before, one of the most important requirements the monomers must meet, is a high difference in reactivities of the two reaction sites. For different reasons we are interested in obtaining double substituted monomers where the substituents R and R' are the same. In the other cases a slow conformational change of the polymer chains over long period of time which might lead to "aging" effects of the polymers is conceivable. 2,6-dichloro-p-phenylene diamine is the only commercially available double substituted diamine. We developed a synthesis for another such monomer, 2,6-dimethoxy-p-phenylene diamine. The synthetic scheme is outlined below:



The monomer could be purified by double vacuo sublimation to a polymerization degree of purity, and polymers could successfully be obtained. One slight drawback is its fast, light-catalyzed decomposition. Exceptional care in the purification of the polymers must therefore be applied to avoid decomposition of the material due to uncontrolled reaction of residual monomers contained in them. On the other hand, it should be possible to synthesize a series of derivatives of this monomer where the substituent R changes continually in its steric hindrance (-OMe, -OEt, -OBu).

4. Determination of Kinetic Parameters

In this last period of funding we determined all the relevant kinetic parameters k_a , r , g_a and g_b ourselves by reacting model compounds and quantifying the products. Earlier we had used values for these parameters published in a paper by Stubbs and Hinshelwood [4]. These values turned out to be quite inaccurate, probably due to the solvent-dependence of these parameters. Values for r , g_a and g_b were obtained according to the method outlined in our last report. The parameters g_a and g_b relate to the symmetric monomer. Parameter g_a defines the ratio of the reaction rate constant of the second functional group on the symmetric monomer after the first functional group has reacted with an $-aX$ group (the faster reacting group) to that of the first functional group reacting. The definition of g_b is analogous to that of g_a . k_a is the rate constant of the slower reacting functional group with terephthaloyl chloride. Approximate values for k_a were obtained experimentally by reacting benzoyl chloride with the corresponding substituted aniline under polymerization conditions. Pseudo-first-order reaction conditions were chosen by using a large excess of benzoyl chloride compared to the substituted aniline. In a typical experiment 10^{-4} moles of benzoyl chloride were added as a powder to 100 ml of a $2 \cdot 10^{-2}$ M solution of diamine in NMP/THF 10:1 with 5% LiCl w/w. The solution was shaken thoroughly and the absorption at 520 nm was measured as a function of time. Kinetic constants for the reaction were calculated from the equation

$$k[Y_{cc}] (t_i - t_1) = \ln (D_1 - D_e)/(D_i - D_e)$$

where $[Y_{cc}]$ is the concentration of benzoyl chloride, t_1 is the time when absorption was started to be measured, D_1 is the absorption at time t_1 , D_e is the absorption at the end of the reaction and D_i is the absorption at the time t_i .

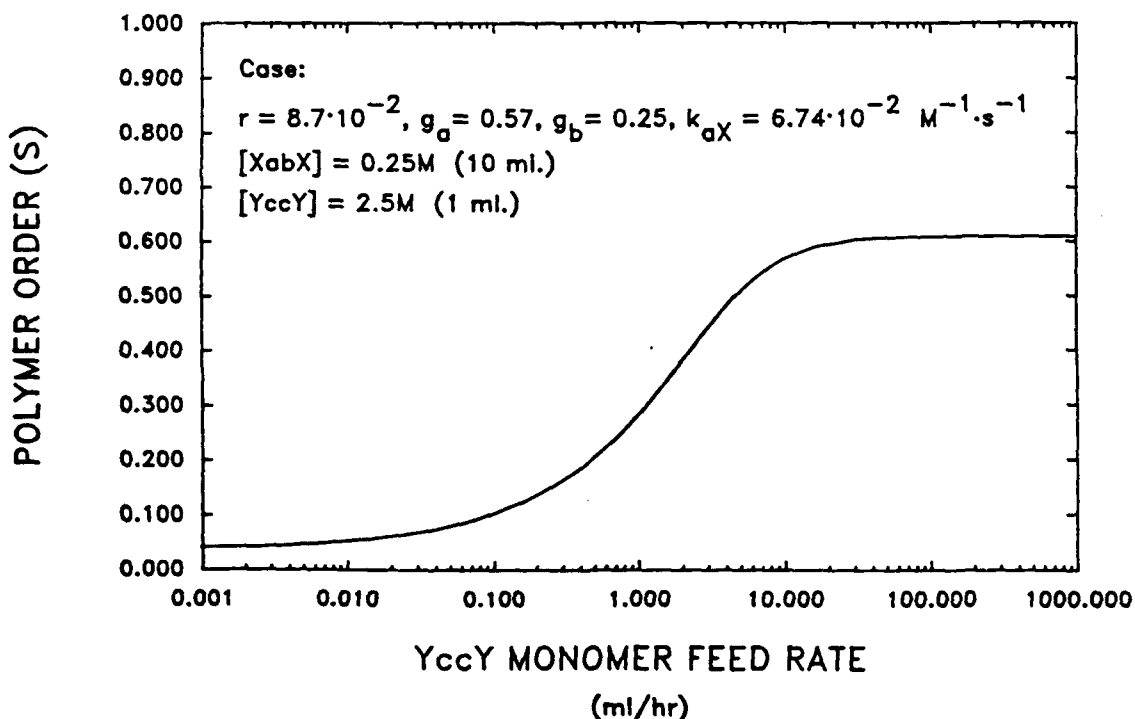
In the table below all the values for the parameters obtained are summarized:

| Substituent R | R' | r | k_a $\times 10^2$ [M s] | g_a | g_b |
|-------------------|-----|--------|---------------------------------|-------|-------|
| -Cl | -Cl | 0.0092 | 5.34 | 0.5 | 0.2 |
| -NO ₂ | -H | 0.0087 | 6.74 | 0.5 | 0.25 |
| -OCH ₃ | -H | 0.0104 | 8.53 | 0.55 | 0.3 |

5. Computer Calculations

In the beginning of this project we made the assumption that there should be no sizable difference in reactivity between a -YccabX- and a -YccbaX- unit, i.e. there should be no influence of the position of the substituent on the reactivity of the acid chloride moiety. We therefore worked with a computer model using only one parameter g to describe the reactivity ratio of the reacted symmetric unit to the non-reacted symmetric unit ($g = g_a = g_b$). Our experiments with model compounds showed, though, that the position of the substituents has a considerable influence on the reactivity of the acid chloride group. We therefore further refined our computer model allowing for differences in values between g_a and g_b . This enabled us to calculate values for s for real processes the way they are employed in the lab. The figure below shows a graph of s versus the monomer feed rate for the poly(2-nitro-p-phenylene-terephthalamide) compound.

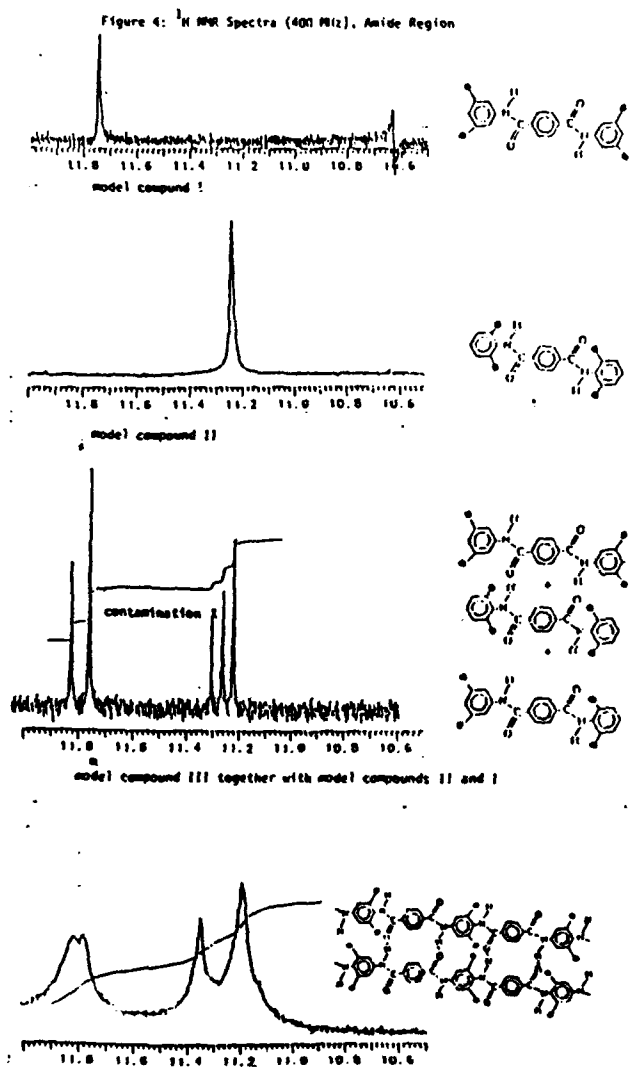
POLYMER ORDER V. YccY MONOMER FEED RATE
Poly(2-nitro-p-phenylene-terephthalamide)



6. Characterization of Polymers

6.1. Determination of Structural Order

In the previous funding period we were able to recognize qualitative differences in the nmr spectra of ordered and random polymers. During the last year we significantly improved our nmr techniques, and we are now able to determine the order parameter s in many cases. This improvement was achieved through better purification of the polymers after synthesis which reduced considerably the peak broadening of the amide protons due to fast exchange with the solvent, use of stronger fields (400-MHz- ^1H -nmr) and the synthesis of model compounds. In the figure below a partial spectrum of a polymer is shown and compared to spectra of its model compounds. Peak assignment was made by direct comparison of the resonances in the polymer spectrum with the corresponding peaks of the model compounds. Values for the order parameter s of the polymer can easily be obtained by calculating the ratios of the peak integrals. With increasing molecular weight the resonances broaden substantially (a phenomenon commonly observed) and only two peaks appear in the amide region. Model compounds for all the polymers investigated were synthesized and characterized, so that a reliable peak assignment is possible for all our systems.



6.2. Vapor Pressure Osmometry (VPO)

In order to obtain some information about the dimensions of the polymers VPO measurements were performed on some selected samples. The usually employed solvents were not suited for our purposes because of their low solvating power, whereas "good" polymer solvents as N-ethylpyrrolidone (NEP) decomposed rapidly under the conditions used for measurement. A workable compromise could be found by using DMF. This solvent is powerful enough to dissolve our polymers and gives reasonably stable readings (in a very narrow temperature range). Due to the inherent limitations of this method and the limited solubility of the polymers only the lower molecular weight samples could be analyzed.

6.3. Size Exclusion Chromatography (SEC)

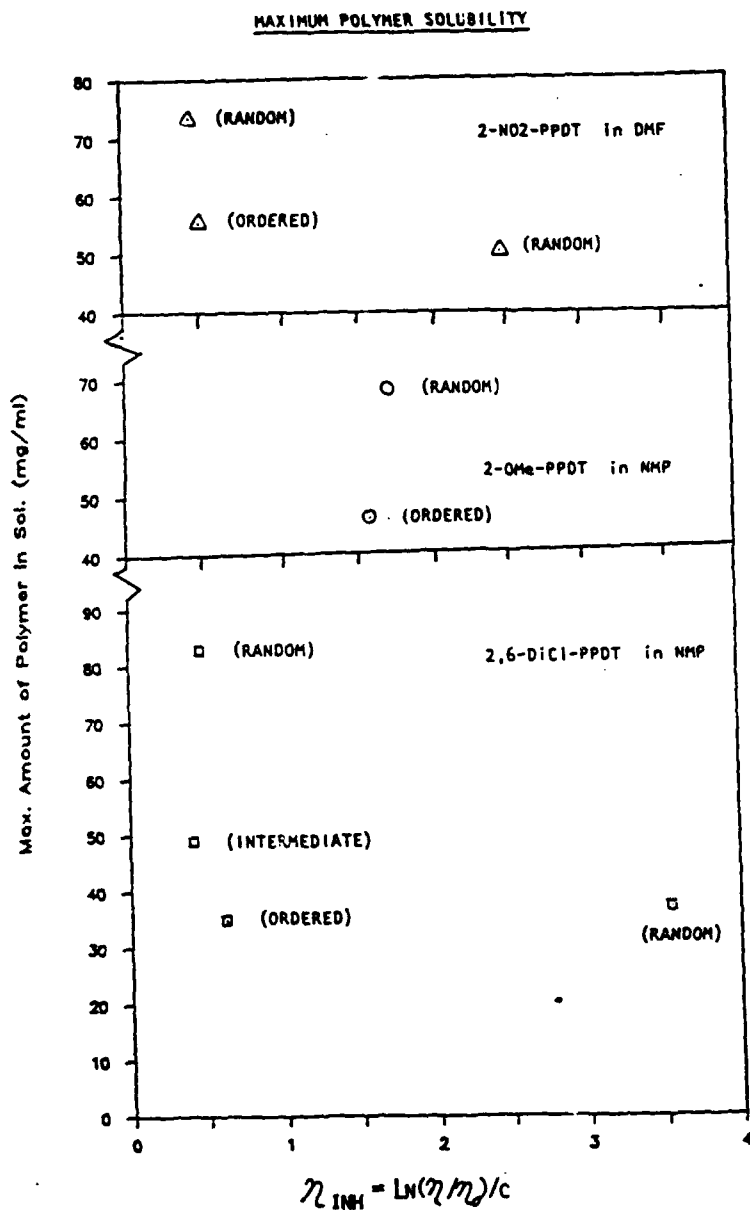
Size exclusion chromatographs of some of our sample were obtained. Using the method published by Strazielle et. al [5], which relies on shape analysis of the peaks, values for the polydispersity (M_w/M_n values) were calculated. All the samples measured showed M_w/M_n values around 2, which corresponds to expectation.

7. Liquid Crystal Behavior

The onset of a nematic phase for some of the polymers synthesized has been determined both experimentally and theoretically. Comparisons have been made for all three types of aramides in both ordered and random forms. From these experiments we were able to conclude that the polymers investigated here retain the essential rigid-rod characteristics of unsubstituted aramides, without substantial "softening" of the amide groups, or conformational distortion of the chain.

8. Polymer Solubilities

Solubility measurements for all the types of polymers with different order parameters s were measured in different solvents. Ordered polymers exhibited much lower solubilities than their more random counterparts with comparable molecular weight. In the table below some results are summarized.



9. Selected Results

In the table below some results selected compounds are summarized.

| Polymer Code | s ¹ | Viscosity n _{inh} (dl/g) ² | M _w /M _n (SEC) | M _n (VPO) (g/mole) | C | H | EM ³ N | Cl | V _p [*] |
|--------------|----------------|--|---|-------------------------------------|-------|------|----------------------|-------|-----------------------------|
| | ±0.05 | ±0.08 | x10 ⁻³ | | | | | | ±0.07 |
| DCP1 | 0.60 | 0.50 | 1.39 | 2.0 | 54.43 | 2.66 | 9.13 | 24.02 | 0.35 |
| DCP2 | 0.23 | 0.48 | 1.50 | 1.8 | 54.22 | 2.12 | 9.18 | 23.22 | 0.38 |
| DCP3 | R | 3.51 | 2.12 | 7.7 | 54.43 | 2.25 | 9.13 | 22.08 | 0.48 |
| DCP4 | R | 4.51 | ----- | --- | 54.89 | 2.22 | 9.17 | 23.19 | ----- |
| DCP5 | 0.53 | 1.12 | 1.57 | 3.7 | 54.14 | 2.78 | 9.11 | 23.18 | 0.10 |
| DCP6 | 0.57 | 0.77 | 1.55 | 2.7 | 54.78 | 2.12 | 9.89 | 23.22 | ----- |
| DCP7 | 0.58 | 0.42 | 1.32 | 1.8 | 54.12 | 2.12 | 9.48 | 23.09 | ----- |
| DCP8 | 0.26 | 1.03 | 1.87 | 2.8 | 55.21 | 2.78 | 9.22 | 22.19 | ----- |
| DCP9 | OR | 1.86 | 1.89 | 4.9 | 54.77 | 2.66 | 9.18 | 21.09 | ----- |
| DCP10 | 0.07 | 0.51 | 1.67 | 1.7 | 54.11 | 2.79 | 9.12 | 23.74 | ----- |
| DCP11 | 0.52 | 0.44 | 1.70 | 1.5 | 55.55 | 2.31 | 9.48 | 21.87 | ----- |
| DCP12 | 0.57 | 0.33 | 1.57 | 1.2 | 52.43 | 2.12 | 9.23 | 22.12 | ----- |
| DCP14 | R | 5.68 | ----- | --- | 54.76 | 2.11 | 9.14 | 22.49 | 0.07 |
| NP1 | 0.52 | 0.50 | 1.55 | 1.8 | 58.71 | 3.16 | 14.26 | | 0.32 |
| NP2 | 0.17 | 0.62 | 1.70 | 2.1 | 58.45 | 3.13 | 14.22 | | 0.35 |
| NP3 | R | 2.55 | 2.09 | 6.2 | 59.21 | 3.18 | 14.84 | | 0.06 |
| NP10 | R | 2.97 | 2.07 | 7.1 | 58.81 | 3.58 | 14.43 | | ----- |
| NP11 | 0.32 | 1.75 | 2.11 | 4.3 | 59.19 | 3.16 | 14.12 | | 0.11 |
| MP1 | 0.57 | 1.89 | 2.12 | 5.6 | 67.09 | 4.61 | 10.23 | | 0.06 |
| MP2 | 0.13 | 1.67 | 2.02 | 5.3 | 67.55 | 4.45 | 10.29 | | 0.13 |
| MP3 | 0.27 | 0.89 | 1.55 | 3.9 | 68.65 | 4.12 | 10.11 | | 0.16 |

¹Where possible actual s measurements are listed, else the codes R, I, OR refer to random, ordered and intermediate polymers, respectively and are assigned based on monomer feed rates.

³Calculated elemental analysis:

DCP: C 54.75%, H 2.63%, N 9.12%, Cl 23.09%

NP: C 59.37%, H 3.20%, N 14.84%

MP: C 67.16%, H 4.51%, N 10.44%

²@ c = 0.05 g/dl in 96% sulfuric acid

The following codes are used:

DCP for poly(2,6-dichloro-p-phenylene terephthalamide)

NP for poly(2-nitro-p-phenylene terephthalamide)

MP for poly(2-methoxy-p-phenylene terephthalamide)

10. Conclusions

Three different types of modified aramides were synthesized with varying degrees of constitutional isomerism. Constitutional isomerism affects profoundly some properties as solubility and crystallinity of these polymers whereas their rigid-rod-character, which is the base of their desirable mechanical properties, is maintained.

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