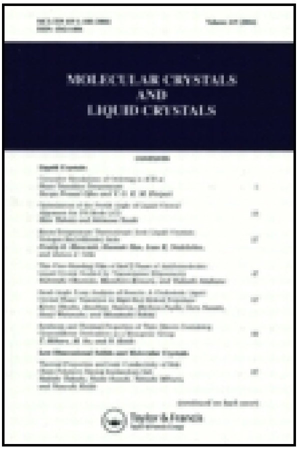

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Optical Properties of Lyotropic LC Polymers

Tatiana V. Filippova [a] & Irina N. Shtennikova [a]

[a] Institute of Macromolecular Compounds of Russian Academy of Sciences, St.-Petersburg, Russia

To cite this article: Tatiana V. Filippova & Irina N. Shtennikova (2001): Optical Properties of Lyotropic LC Polymers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 359:1, 177-184

To link to this article: http://dx.doi.org/10.1080/10587250108035579

Mol. Cryst. and Liq. Cryst., 2001, Vol. 359, pp. 177-184
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Printed in Malaysia

Optical Properties of Lyotropic LC Polymers

TATIANA V. FILIPPOVA and IRINA N. SHTENNIKOVA

Institute of Macromolecular Compounds of Russian Academy of Sciences, St.-Petersburg, Russia

Polyalkylisocyanates so as aromatic polyamides have great importance for their ability to show liquid crystal properties. And so many of them are used for very high – strength synthetical fibre materials. This work deals with delute solutions of polyisocyanates, their copolymers, aromatic polyamides and macromolecules with heterocycles in main chain. Hydrodynamic and optical properties of these polyamides are investigated by viscometry and flow birefringence methods. Experimental results are compared with those for different polyamides studied. LC macromolecules show rigid worm – like chains behavior.

Keywords: aliphatic and para-aromatic polyamides; flow birefringence; intrinsic viscosity

1. INTRODUCTION

Recent years investigations of different polyamides containing only amide groups in their main chain (polyalkylisocyanates) [1, 2] and combination of amide groups with phenyl rings (poly-para-benzamide, poly-para-phenyleneterephthalamide) [3] and different heterocycles (polyamidobenzimidazole, polybiphenylsulphoneterephthalamide) [4, 5] show that all of them formed an ordered liquid-crystalline phase in concentrated solutions. To explain the lyotropic LC behavior of these polyamides it is necessary to know the characteristics of their individual molecules. For these purpose optical and hydrodynamic properties of polyamides were investigated in a wide range of molecular weights in very delute solutions characterizing the macromolecules itself. Such quantitative data as flow birefringence $[n]/[\eta]$ and intrinsic viscosity $[\eta]$, macromolecular rigidity (Kuhn segment length) and conformation are determined in our work. Most of investigated polyamides were soluble only in concentrated sulfuric acid, so a special technique of flow birefringence measuring was used.

2. EXPERIMENTAL

Flow birefringence was measured using visual optical methods [3] in dinamooptimeter with an internal rotor. The height of the rotor was 3 cm and the gap between the stator and the rotor was 0.054 cm. All the solutions exhibited birefringence Δn linearly depending on the flow rate gradient g (Figure 1). The $\Delta n/g$ values are obtained from the straight lines $\Delta n = f(g)$ slope (see Figure 1). The values of characteristic birefringence $[n]/[\eta]$ were determined by extrapolation to zero concentration $c \to 0$ and rate gradient $g \to 0$ values of reduced flow birefringence $\Delta n/g(\eta - \eta_0)$, here η, η_0 are solution and solvent viscosities. Intrinsic viscosities $[\eta]$ were determined in capillary Ostwald viscometer. The values of $[\eta]$ and $[n]/[\eta]$ are shown in the Table 1.

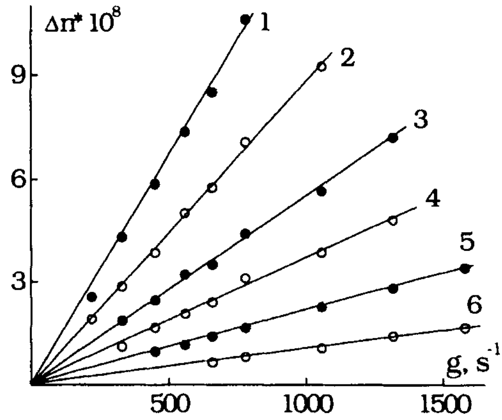
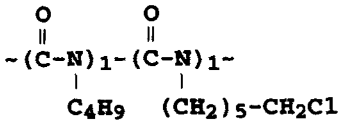
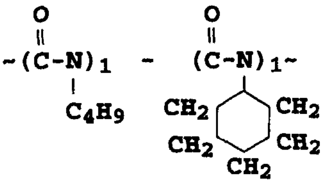
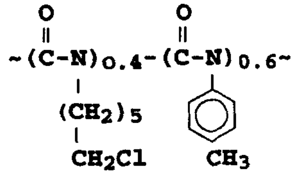
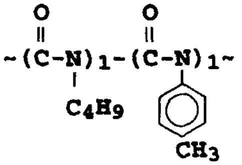
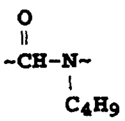


FIGURE 1. Dependences of birefringence Δn on rate gradient g for copolymer No. 1 (polybutylisocyanate with polyhexylisocyanate) in tetrachloromethane, concentrations of solutions are 0.455 (1), 0.283 (2), 0.195 (3), 0.125 (4), 0.065 (5), and 0.047 (6) g/dl.

3. RESULTS AND DISCUSSION

Optical and conformational properties of the macromolecules of copolymers of some polyisocyanates investigated by methods of viscometry and flow birefringence shown in Table 1 allows to make conclutions that the [n]/[η] values depend on chemical structure of the side chain. Consequently, the equilibrium rigidity of polyisocyanates investigated is function of the side substitutes types.

TABLE 1. Intrinsic viscosities [η] and flow birefringence [n]/[η] of polyisocyanates and its copolymers in tetracloromethane (No.1, 2, 5, 6) and acetone (No.3, 4, 7).

	Polymer	[η], dl/g	[n]/[η]×10^{10}, g^{-1}×cm×s^{2}
1.	 $\sim(\overset{\overset{O}{\|}}{C}-\underset{\underset{C_4H_9}{\|}}{N})_1-(\overset{\overset{O}{\|}}{C}-\underset{\underset{(CH_2)_5-CH_2Cl}{\|}}{N})_1\sim$	1.95	100
2.		2.60	250
3.		0.38	- 1.7
4.		0.15	- 15
5.	 $-\overset{\overset{O}{\|}}{C}H-\underset{\underset{C_4H_9}{\|}}{N}\sim$	3.8	220

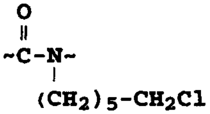
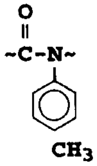
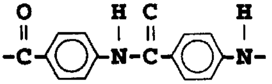
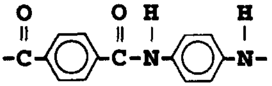
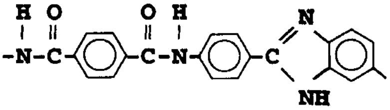
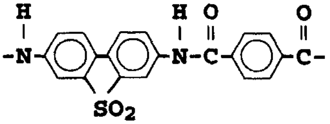
	Polymer	[η], dl/g	[n]/[η]×10^{10}, g^{-1}×cm×s^2
6.	 $-\overset{\overset{O}{\|}}{C}-\underset{\underset{(CH_2)_5-CH_2Cl}{\|}}{N}-$	2.0	200
7.		0.26	- 35

TABLE 2. Hydrodynamical and optical characteristics of para-aromatic polyamides in sulfuric acid.

	Polymer	[η], dl/g	[n]/[η]×10^{10} g^{-1}×cm×s^2
8.		3.0	480
9.		8.5	400
10.		5.6	320
11.		9.0	460

The values of characteristic viscosity [η] of investigated samples are high enough. This fact allows to suppose that measurements of flow birefringence [n]/[η] were carried out in the range of molecular weights where the macromolecules are in Gaussian conformation and [n]/[η] ~ A. Here A is segment Kuhn length and is characteristic of equilibrium rigidity of macromolecular chain. The results obtained for copolymers (No. 1 - 4) are compared with those for polyisocyanates (No. 5 – 7). Macromolecules of polyisocyanates with alkylene side substitutions (polymers No. 5 and 6 in Table 1) are characterized by the high equilibrium rigidity, which is due to quasi-conjugation of valence bonds in amide group of their main chain. The conjugation may be influenced by the phenylene substitutions (polymer No. 7 in Table 1). We have shown that even content of aromatic component in solvent influenced the polyisocyanates equilibrium rigidity when investigated macromolecules were dissolved in mixture of tetrachloromethane and pentafluorophenol) [6].

The analysis of experimental results shows that copolymers with phenylene substitution (copolymers No. 3 and 4 in Table 1) are characterized by low intramolecular order and high flexibility of the polymer chain. This fact is confirmed by the small and negative values of flow birefringence [n]/[η] of their solutions.

In the cases where substitutions have no aromatic component (copolymers No. 1 and 2 in Table 1) the chain is rigid and molecular order is very high. It can be seen that hexyl side group does not influence the conjugation as it is in the case of phenylene side group (copolymers No. 3 and 4). The flow birefringence of copolymer No. 1

is a little less than it can be wait to be. This fact may be explained by some defects in polyhexylisocyanates chains which make it more flexible than polybutylisocyanate ones [2, 3].

Results of flow birefringence investigations of aromatic amides in sulfuric acid solutions [3 – 5] are represented in Table 2 for macromolecules containing in their main chain not only amide groups but also phenylene rings in para-postion and hetero-rings. High positive birefringence and, consequently, high molecular order are due to crankshaft conformation [3], which is connected mostly with planar trans-configuration of amide group. So such molecules are characterized by exceptionally high equilibrium rigidity, which is influenced of cause by some defects in amide group (inequality of angles at carbon and nitrogen atoms), thermal motion of the chain destroying coplanarity, presence of cis-configurational amide groups. Real chains are different by its rigidity due to some individual properties.

4 CONCLUSIONS

The high equilibrium rigidity of investigated polymers favors the formation of the lyotropic mesomorphic (liquid – crystalline) structure in their concentrated solutions. This phenomenon is used to obtain ultrahigh modulus fibers from such synthetic polymers as various polyamides and polyesters [7]. The potential of the polymer for lyotropic mesomorphism was found to be directly dependent on the equilibrium rigidity of its molecules characterized by birefringence values and Kuhn segment length.

5. ACKNOWLEDGEMENTS

This research has been supported by Federal program INTEGRATION (Grant No. 326.88).

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