NEW HETEROCYCLIC POLYMERS
WITH VICINAL PARABANIC STRUCTURES

Elena SCORTANU[*] and Cristina PRISACARIU

The Roumanian Academy's Institute of Macromolecular Chemistry "Petru Poni"
Aleea Grigore Ghica Voda Nr. 41 A, Iaşi, 700487 Roumania

The paper deals with the study of heterocyclization via the cyclocondensation reaction of some reactive polymers by using oxalyl chloride. A few polymers and model compounds were synthesized by the polyaddition reaction of some isocyanates and hydrazine. The products have been characterized by elemental analyses, IR spectroscopy, thermogravimetry (TGA), differential scaning calorimetry (DSC), solubility, viscosity and gel permeation chromatography measurements (GPC). The parabanic structure formation was studied as results from the cyclocondensation reaction of obtained polyurylenes and oxalyl chloride. The influence of reaction conditions on the heterocyclization process was discussed. An evaluation of the transformation degree was made by using the IR spectroscopy. The synthesized polymers presented the thermal stability up to 260 – 350°C and viscosity values between 0.2 – 0.6 dl/g.

INTRODUCTION

The polymers containing 1,3-imidazolidine-2,4,5-trione rings on the macromolecular backbone are known as poly(parabanic acid)s and represent a relatively new class of thermoplastic polymers useful as electro-insulating materials in electronic industry. There are known two methods to obtain this kind of polymers starting from diisocyanates. One of them is based on the polyaddition reaction of diisocyanates with hydrogen cyanide followed by hydrolysis,[1] the second method consists in a polyaddition-polycondensation reaction between diisocyanates and bisesteroxalamides.[2] In previous papers we described preliminary original data concerning the parabanic polymers obtained by an intermolecular reaction between polyureas and oxalyl chloride.[3-5]

The present study deals with poly(parabanic acid)s syntheses starting from an unusual kind of polymer which contains biurea groups in the main chain. Such polymers were first time obtained by Campbell (1959) and Farago (1961) by the reaction of some diisocyanates with hydrazine hydrate in dimethylformamide or in other solvents, even in dioxane/water using triethylamine as catalyst.[6,7] The authors named these linear polymers as poly(urylenes). Based on the previous experience we have obtained some heterocyclic structures by the polymer analogue reaction between a few aromatic poly(urylenes) synthesized from 4,4'-diphenylmethane diisocyanate, 4,4'-diphenylether diisocyanate or 2,4-toluylen diisocyanate with hydrazine hydrate. We studied the cyclocondensation reaction firstly on a model compound: hydrazin-N,N'-dianilid formyl prepared from phenyl isocyanate and hydrazine hydrate, and then on poly(urylenes) by varying the reaction conditions.

[*] Corresponding author: nutiscor@yahoo.com

RESULTS AND DISCUSSION

Our earlier investigations showed the possibility to obtain parabanic structures on the model compounds and polymers.[3-5] The polyureas containing mainly para-substituted aromatic structure suffer only a partial cyclization[3-5] with different degrees of transformation.[8] The heterocyclization reaction was quantitatively occured in dry solvents at 50-60 °C in the presence of an acceptor like pyridine only for model compounds or flexible polyureas. This is explained

by the solubilities of the products in the reaction solvent. In the present work we obtained polymers containing two adjoining parabanic rings by treating polyurylenes with oxalyl chloride by using two chlorinated solvents with different polarity: 1,2-dichloroethane (DCE) and 1,1,2-trichloroethane (TCE). We studied firstly the reaction of cyclo-condensation on the model compound and then on polymers. The reactions are presented in the scheme 1 and 2 and characteristics of products are presented in Table 1.
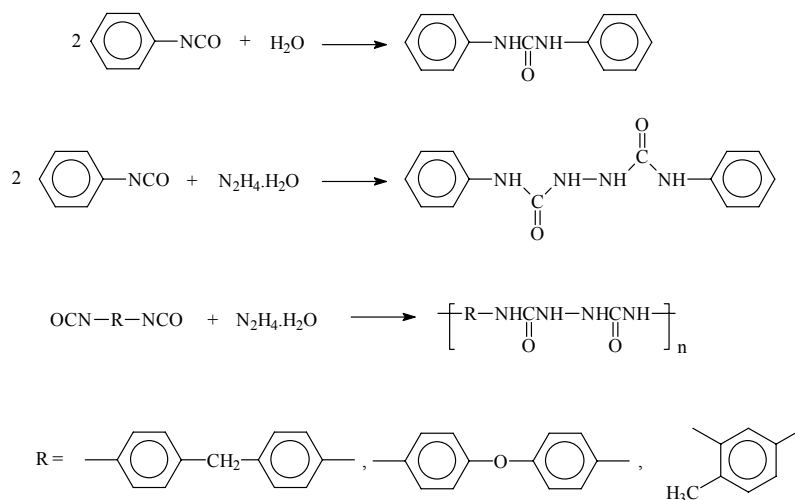
Scheme 1
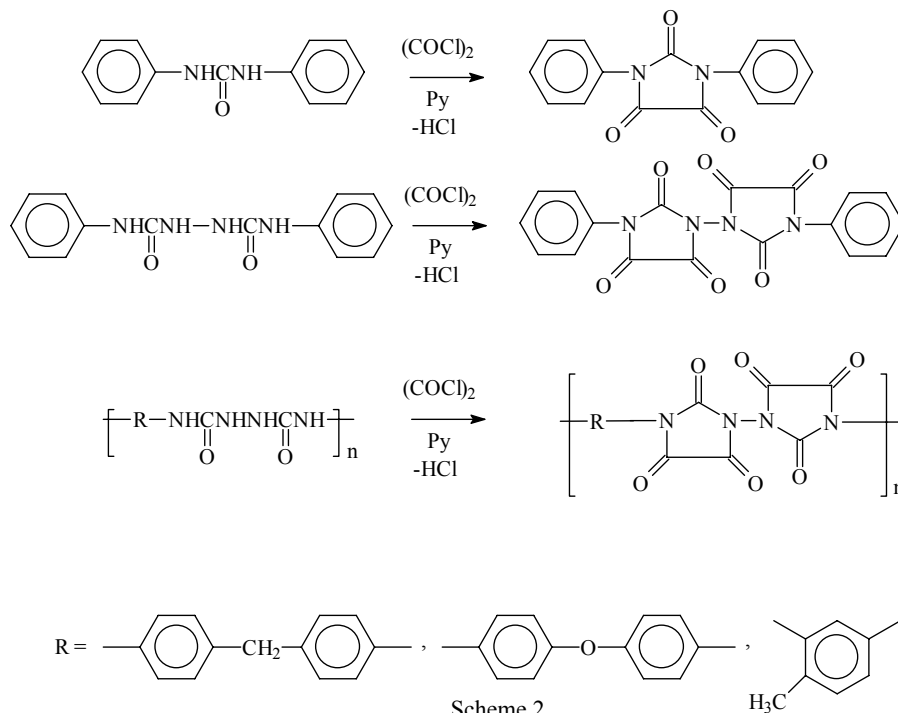
Scheme 2

Table 1
Characterization of polymers and model compounds

Product	Solubility					η_{inh} (dL/g) (a)	TGA (°C) (b)			M.p. (°C) (c)	DSC (°C) (d)		
	DMF	DMF +LiCl	DMSO	DCE	TCE		T_5	T_{10}	MaxDTG		T_m	T_g	T_{decomp}
PhU	±	+	+	−	−		240	250	260;320	257-260	262	−	>310
PhP	+	+	+	±	+		195	265	370	242-244	191	−	>250
PUMDI	−	±	±	−	−	0.60	240	290	305;315	286-293			
PPMDI DCE	±	+	±	−	−	0.26	190	275	350;400	292-310			
PPMDI TCE (insol)	±	+	±	−	−	0.24	135	185	270;365		−	62	195
PPMDI TCE (sol)	+	+	+	−	+	0.16*							
PUODI	−	±	±	−	−	0.54				>355			
PPODI DCE	−	±	±	−	−	0.06	160	245	365	158-306			
PUTDI	−	±	±	−	−	0.48				259-264			
PPTDI DCE	−	±	±	−	−	0.17	255	285	245;390	259-274			
PPTDI TCE (insol)	−	±	±	−	−	0.38	235	285	250;320		−	55	195; 265
PPTDI TCE (sol)	±	+	±	−	±	0.10*		170	190;300; 325		−	60	265

a) Inherent viscosity measured at a concentration of 0.5 g/dL in DMF + 2% LiCl at 20°C; *) viscosity measured at a concentration of 0.5 g/dL in DMF at 20°C.

b) T_5 and T_{10} represent the temperatures of 5% and 10% weight loss; MaxDTG represents the peak(s) of DTG curves corresponding on the inflexion points of TG curves as determined by TGA.

c) Determined in a glass capillary tube.
T_m, T_g and T_{decomp} represent the temperatures of melting, glassy transition and decomposition as determined from DSC curves.

By varying the polarity of solvent (DCE is less polar than TCE), the quantity of pyridine (a few drops until an equimolar ratio vis a vis of HCl evolved) or the time of reaction, we observed an improvement in the cyclization progress that can easily be monitored by IR spectra. Thus, the characteristic bands of diurea groups (ν_{NH} at 3300 cm⁻¹ and ν_{CO} at 1630-1670 cm⁻¹) disappear with the transformation progress while a new strong band characteristic to parabanic rings (ν_{CO} at 1750-1780 cm⁻¹) appears simultaneously. By chosing appropriate absorption bands of aromatic radical we have calculated the transformation degree using an earlier reported method[8] (Table 2). We can observed that soluble oligomers have higher transformation degree than the insoluble polymers, which explain the presence of the strong interchain packing by hydrogen bonds in the insoluble products. The solubilities of parabanic polymers in aprotic solvents (with or without LiCl) are good

and they can be partially dissolved by DCE or TCE. The values of the inherent viscosities decrease, in some cases drastically after the cyclization because of the disappearance of interchain hydrogen bonds, of some extent, or due to depolymerizations. For example, polyurylenes have viscosities of 0.48 dL/g (PUTDI), 0.54 dL/g (PUODI) and 0.60 dL/g (PUMDI). Polyparabanates synthesized in DCE have viscosities of 0.26 dL/g (PPMDI), 0.17 dL/g (PPTDI), but only 0.06 dL/g in the case of PPODI. By using TCE as solvent the viscosity values increased in the case of PPTDI (0.38 dL/g) or have the same value like in the case of PPMDI (0.24 dL/g). It can observe that the values of viscosity in DMF+LiCl are higher (polymers are almost entirely disolved) than those determined in DMF. The explanation is that the polymers are not entirely soluble in DMF but only oligomers, because of oligomers smaller molecular mass and the differences of chemical structures (more parabanic rings).

Table 2

Transformation degrees calculated from the absorbance of representative groups determined by IR spectroscopy

Polymer	Urea groups		Parabanic ring	Aromatic ring	Method		Transformation degree %
	$A_{3260-3280}$	$A_{1650-1670}$	$A_{1730-1780}$	$A_{1480-1520}$	A_{1670}/A_{1500}	A_{3260}/A_{1480}	
PUMDI	0.107	0.341	–	0.445	0.766		
PPMDI DCE	0.073	0.215	0.258	0.440	0.4886		36.21
PPMDI TCE (5h)	0.043	–	0.424	0.360	0.119		50.42
PPMDI TCE (10 h) (insol)	0.034	–	0.434	0.383	0.0887		63.04
PPMDI TCE (10 h) (sol)	0.049	–	0.690	0.529	0.0926		61.42
PUODI	0.15	0.285	–	0.444	0.642	0.338	
PPODI DCE	0.054	0.105	0.300	0.665	0.1579	0.0812	75.40; 75.975
PUTDI	0.093	0.390	–	0.302	1.29		
PPTDI DCE	0.134	0.230	shoulder	0.215	1.06976		17.07
PPTDI TCE (4 h)	0.130	0.135	0.108	0.237	0.5696		55.84
PPTDI TCE (14.5 h) (insol)	0.13	0.175	shoulder	0.197	0.8883		31.14
PPTDI TCE (14.5 h) (sol)	0.071	0.108	0.725	0.316	0.34177		73.51

The degree of transformation was calculated as: $T = 100 \times (a-a')/a$, where **a, a'** = A_{urea}/A_{arom} of polyurylenes (**a**) and of parabanic polymers (**a'**).

The polyparabanates were tested by GPC also, DMF and DMF+LiCl being used as eluents. As shown in Table 3 molecular values (Mn and Mw) are higher when the eluent is DMF, contrary with the case of viscosity measurements. For example PPMDI in DMF had Mw(11198), Mn(9334) and 1.2 polydispersity while in DMF+LiCl had Mw(1854), Mn(1663) and 1.11 polydispersity. The explanation could be the fact that DMF cannot dissolve entirely the partially transformed polymers which contain a significant number of interchain hydrogen bonds that can produced associates in solution. There are known associates of some urea compound oligomers that in poor solvents can form supermolecular associates named supermolecular polymers.[9] The elemental analyses of C and H confirm the proposed structures but the N analyses are poor probably because of labile linkage between nitrogen atoms. The thermal behaviour of parabanic polymers was described in Table 1, by means of thermogravimetric analyses and differential scanning calorimetry of both polyurylenes and polyparabanates as well as by melting domain measurement's data (determined in glass capillary). The thermal stability of transformed polymers decreased in some cases with above 50 °C. This fact is determined by the presence of the two parabanic rings bonded by labile N-N linkage. Poly(parabanic acid)s presented glass transition temperatures between 55-62 °C.

EXPERIMENTAL PART

Materials

Commercial phenyl isocyanate (PI), 2,4-tolylene diisocyanate (TDI), 4,4'-diphenylmethane diisocyanate (MDI) and 4,4'-diphenylether diisocyanate (ODI) were purified in the usual manner. Commercial hydrazine hydrate was used without purification. Commercial oxalyl chloride was used as received. Commercial solvents dimethylformamide (DMF), 1,2-dichloroethane (DCE) and 1,1,2-trichloroethane (TCE) were freshly distilled. The organic solvents like methanol, acetone, ethyl ether, petroleum ether were used as received.

Synthesis of the model compound

Diphenyl urea and diphenyl parabanic acid were obtained as earlier described.[3,4] Hydrazin-N,N'-dianilid formyl (N,N'

diphenyl biurea (PhU)): a solution of 0.5 mL [0.505 g (0.0101 mols)] hydrazine hydrate in 5 mL DMF was added by dripping on a ice-cold solution of 2.4 mL [2.592 g (0.02178 mols)] phenyl isocyanate in 5 mL DMF. The product was obtained immediately as a precipitate, filtered, washed with methanol and dried at 100 °C.

Diphenyl-diparabanate (PhP): at a suspension of 1 g (0.0037 mols) diphenyl biurea in DCE and 3-4 drops of pyridine, 2.5 mL [3.745 g (0.0295 mols)] oxalyl chloride was added dropwise under stirring at the room temperature. The reaction mixture was then heated 5 h at 55-65 °C. After first two hours the mixture became clear. The solution shows a yellow colour. The solvent was removed by distillation at reduced presure because of the pronounced tendence to form dark resins. By changing the solvent DCE to the most polar TCE it can reduce the resins formation and, in this way, the reaction became almost complete (yield 94.21%).

Synthesis of polymers

Polyurylenes (PU). A solution of 0.025 mols of hydrazine hydrate in 5 mL DMF was added dropwise, under stirring, to a cooled solution of 0.025 mols of a diisocyanate in 25 mL DMF. An exothermic reaction was observed and the mixture became a very viscous solution or the polymer precipitated immediately. The mixture was diluted with a supplement of 25 mL DMF (optionally LiCl) and stirred one hour. The resulted product was poured into methanol, filtered, washed with methanol and dried at 100 °C.

Polyparabanates (PP). To a stirred suspension of a polyurylene (0.005 mols) in 50 mL anhydrous DCE or TCE containing variable quantities of pyridine, 2 mL [2,996 g (0.0236 mols)] oxalyl chloride was added at the room temperature. The mixture was then heated a few hours (5-15) at 55-65 °C. The progress of reaction was followed by IR spectra. The product was isolated by pouring into 200 mL methanol, filtered, washed with methanol and dried at 100 °C. The characteristics of polymers are shown in Table 1.

Measurements

Thermogravimetric analyses of polymers (TGA) i.e. differential thermal gravimetry (DTG) were performed with a MOM Budapest derivatograph in air at a heating rate of 6-12 °C/min. The differential scanning calorimetry (DSC) data was obtained with a Mettler DSC 12 E with a heating rate of 10 °/min in a nitrogen atmosphere. IR spectra of polymers were recorded with a Perkin-Elmer using KBr pellets. The inherent viscosities of 0.5% polymers solutions in appropriate solvents at 20 °C were measured with an Ubbelohde viscometer. In order to obtain molecular mass values gel permeation chromatography tests were performed on Evaporative Mass Detector type PL-EMD 950 (polystyrene calibration).

Table 3

GPC polymers characterizations

Polymer	η_{inh} (dl/g) a)	η_{inh} (dl/g) b)	GPC a)			GPC b)		
			Mn	Mw	Ps	Mn	Mw	Ps
PPMDI	0,16	0,24	9334	11198	1,20	1663	1854	1,115
PPTDI	0,10	0,38	6830	8131	1,19	1642	1889	1,150
PPODI	0,06	-	-	-	-	2047	2242	1,095

a) Represent polymer solutions in DMF;
b) Represent polymer solutions in DMF+LiCl.

CONCLUSIONS

Parabanic polymers described in this paper presented good thermal stabilities (T_{10} between 180-290 °C, Max DTG of 250-400 °C) and also Tg of 55-62 °C. Polyurylenes have good viscosity values that decrease after the cyclocondensation process because of the disappearance of interchain hydrogen bonds or even some depolymerization processes. The possibility of heterocyclization process was demonstrated and using the spectral data we succeeded in calculating the transformation degree.

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