

Synthesis and Characterization of Some Oligopolyalkylene–Polyamines

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ABSTRACT: The reaction of diamines with dihalides in basic medium was carried out, leading to the formation of different varieties of both cyclic and acyclic products. In this work, the reaction was directed to form mainly one of them by reacting different diamines with both dichloroethane and dichloromethane as alkylating agents, using two techniques which were compared with each other. The obtained oligomeric products were characterized by using spectroscopic and elemental analyses. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1009–1013, 1997

INTRODUCTION

Polyalkylene–polyamines have been previously synthesized by reaction of aromatic amines with alcohols, and required a pressure of 80 bar and a high temperature (280°C).¹ Alkyl chlorides can react with aromatic amines in the presence of catalysts such as lithium amide,² lithium–naphthalene complex,³ and ion-exchange resins.⁴ Recently, some chloroalkylaryl amines were prepared by reacting aromatic amines with polychloroalkanes in presence of stannous chloride and hydrochloric acid in methanol at 50–60°C.^{5–10} Moreover, these polymers were found to be useful in many different applications.^{11–16}

EXPERIMENTAL

All solvents, as well as ethylenediamine, were purified according to the standard methods.¹⁷ The diamines were purified by crystallization from ethanol. FTIR spectroscopic analysis was by means of a Mattson 5000 FTIR spectrophotometer. ¹H-NMR spectra were recorded on a Varian

EM-390 spectrometer (90 MHz). Elemental microdetermination was carried out using a Perkin-Elmer 2400 series II CHNS/O Autoanalyzer.

Synthesis

Method (A):

A solution of 10 mmol of the diamine *Ia–c* in toluene, 3.0 g sodium bicarbonate, and ~ 2.0 ml of the dichloroalkane *IIa* and *b* were mixed with stirring and refluxed at about 115°C for 36 h. After cooling to room temperature, the reaction mixture was poured into icewater and neutralized with 2 *N* hydrochloric acid. The unreacted diamine was removed through the isolation of the organic phase. The obtained products (*IIIa–VIIIa*) were salted out using a saturated solution of sodium chloride. The products were washed with a slight amount of water (2× ~ 5 mL), and then thoroughly washed with methanol, acetone, and finally with diethylether (3× ~ 10 mL each). The hydrochloride form was neutralized with 10% sodium bicarbonate solution into the basic form (*IIIb–VIIIb*), which was filtered off and dried in vacuum at 70°C overnight. All products were dark green, soluble in both *N,N*-dimethylformamide (DMF) and di-

methyl sulfoxide (DMSO), and melted above 300°C.

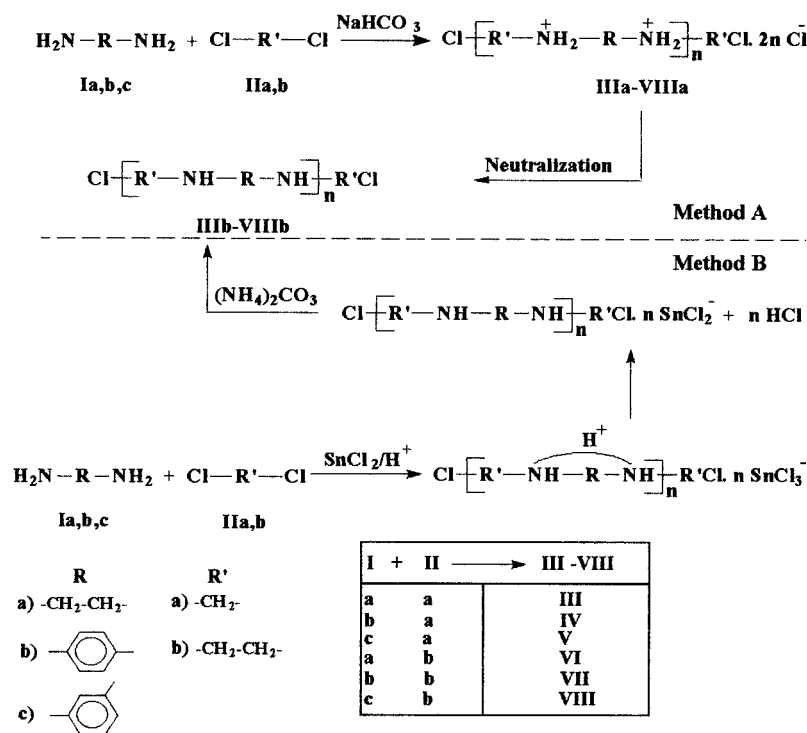
Method (B):

To a solution of 10 mmol of the diamine in 25 mL methanol, about 25 mL HCl (10 *N*) was added dropwise under reflux and with continuous stirring. About 3 g (26 mmol) tin dust was added slowly at 77°C with stirring for 1 h. Afterward, ~3 mL of the dichloroalkane was also added dropwise to the methanol solution at 55°C with stirring over a period of 2 h followed by 8 h further stirring at 55°C. After cooling to the room temperature, the formed precipitate was filtered off and treated with a solution of 3 g (30 mmol) ammonium carbonate in 15 mL water with stirring and refluxed at 100–110°C for 12 h to precipitate tin as tin carbonate. After the addition of ~40 mL water, the mixture was stirred further for 12 h at 60°C. The precipitated tin carbonate was filtered off and the clear solution was evaporated to a dry residue that was extracted with absolute ethanol. The products *IIIa–VIIIa* were obtained after evaporation of the ethanolic solution. The free amine products *IIIb–VIIIb* were regenerated from

the corresponding HCl form by neutralization with 10% sodium bicarbonate solution and isolated by filtration through a sintered glass filter G3 under suction.

RESULTS AND DISCUSSION

The present work is aimed at the synthesis of polyalkylene–polyamines by two techniques and their characterization. One technique involves the reaction of the diamine (*Ia–c*) with a dihalide (*IIa, b*) in the presence of a slightly basic catalyst such as sodium bicarbonate. This resulted in the formation of the oligopolyalkylene–polyamine hydrochloride (*IIIa–VIIIa*), which can be converted into the free base form (*IIIb–VIIIb*) by neutralization with ammonium hydroxide. The other technique involves the reaction of the diamine with a dihalide in the presence of hydrochloric acid and a stoichiometric amount of stannous chloride. It leads to the formation of polyalkylene–polyamine adducts with stannous chloride. The hydrochloride form was obtained by precipitation of tin as tin carbonate using ammonium carbonate. The



Scheme 1 Reaction equations for synthesis of polyalkylene polyamines *III–VIII* under the conditions of methods A and B.

Table I Number Average Molecular Weight (\overline{M}_n); Degree of Polymerization (\overline{DP}) and the Reaction Yield of the Polymeric Samples *IIIb-VIIIb* According to the Two Methods Used for Preparation

Samples	Method A			Method B		
	\overline{M}_n	Yield (%)	\overline{DP}	\overline{M}_n	Yield (%)	\overline{DP}
<i>IIIb</i>	1381	40	18	1886	50	25
<i>IVb</i>	4887	80	40	5847	75	48
<i>Vb</i>	4286	75	35	5367	75	44
<i>VIb</i>	2250	25	25	3197	50	36
<i>VIIb</i>	7473	90	55	9484	82	70
<i>VIIIb</i>	5998	90	44	7070	80	52

free base form was obtained by neutralization with ammonium hydroxide. Ethylene diamine, *m*- and *p*-phenylene diamines were used as diamines, while 1,2-dichloroethane and dichloromethane were the two halides used (Scheme 1). A comparison of the conversion of the diamine between the two techniques is represented in Table I.

Characterization

Infra-red spectroscopic analyses of the obtained oligomeric samples¹⁸ showed absorptions at 2900 and 700 cm^{-1} corresponding to aliphatic CH— and C—Cl stretch, respectively, for all samples, and an absorption at 1510 cm^{-1} corresponding to CH— aromatic for all samples also, except for *III* and *VI*. For samples *IIIa-VIIIa*, the absorptions at 1610 and 1400 cm^{-1} , corresponding to $^+\text{NH}_2$ and C—N⁺, respectively, indicate the presence of oligomers in the hydrochloride form. The weak absorptions at 1600 and 1500 cm^{-1} , corresponding to ^+NH and $^+\text{NH}_3$, respectively, indicate the presence of a minute amount of crosslinking or branching due to double alkylation at one amine center. The absence of the absorbancies corresponding to C—N⁺ from the spectrum of *IIIb-VI-IIb* indicates that these samples are completely free from the hydrochloride centers. On the other hand, $^1\text{H-NMR}$ of the neutralized oligomers *IVb* and *Vb* showed two broad peaks centered at ~ 6.8 ppm and ~ 4.3 ppm, corresponding to aromatic four protons and aliphatic two protons of the CH_2 — group, respectively. The oligomeric products *VIIb* and *VIIIb* also showed two broad peaks at about 6.8 ppm, corresponding to aromatic four protons. There are also two triplet peaks centered at ~ 2.8 and 4.3 ppm, corresponding to aliphatic

four protons of the C_2H_4 group attached to the NH— group and $\text{C}_2\text{H}_4\text{Cl}$ at the end of the chain. There is also a peak located at about 3.2 ppm corresponding to two protons of two NH groups. Figure 1 illustrates the $^1\text{H-NMR}$ spectrum of the neutralized product *VIIb* as an example. The oligomeric products *IIIb* and *VIb* have no peaks at about 6.8 ppm, corresponding to the aromatic protons, but showed peaks at about 3.8 ppm, corresponding to aliphatic six protons of three CH_2 groups present in *IIIb*, and eight protons of four CH_2 groups present in *VIb*.

Determination of Average Degree of Polymerization

The neutralized polymers (*IIIb-VIIIb*) are found to be free from amine—hydrochloride centers as proved by IR spectroscopic analysis. Crosslinking or branching can be neglected as indicated by the very weak absorption at 1600 cm^{-1} of ^+NH . Besides, the absence of absorption at 3390 cm^{-1} , corresponding to NH_2 stretch for neutralized polymers, indicates the presence of —R'Cl groups in

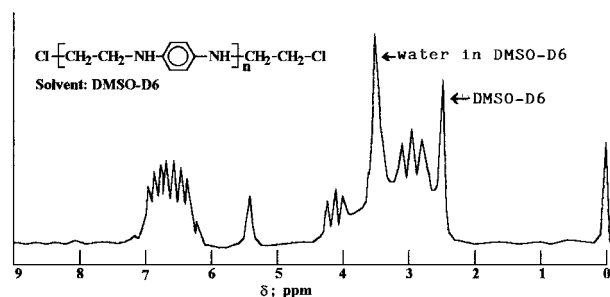
**Figure 1** $^1\text{H-NMR}$ spectrum of the neutralized product *VIIb*.

Table II Elemental Analysis Data of the Polymeric Samples *IIIb-VIIIb* in the Free Base Form Synthesized According to Both Methods A and B

Product	Method A				Method B			
	C	H	N	Cl	C	H	N	Cl
<i>IIIb</i>	47.78	10.65	36.50	5.06	48.36	10.80	37.13	3.71
<i>IVb</i>	69.00	6.64	22.92	1.43	69.16	6.65	22.99	1.20
<i>Vb</i>	68.87	6.63	22.87	1.63	69.09	6.65	22.96	1.30
<i>VIb</i>	54.40	11.38	31.12	3.11	54.80	11.47	31.54	2.19
<i>VIIb</i>	70.98	7.47	20.61	0.94	71.11	7.48	20.67	0.74
<i>VIIIb</i>	70.83	7.46	20.55	1.17	70.94	7.47	20.60	0.99

both chain ends. So, the number average molecular weight (\bar{M}_n) and consequently the average degree of polymerization (\overline{DP}), can be calculated according to the formula $\text{Cl}-[\text{R}'\text{-NH-R-NH}]_n-\text{R}'\text{Cl}$ through microdetermination of chlorine content as end-group analysis technique. The data shown are the arithmetic means of three determinations (Table II). On this basis, the average degree of polymerization (\overline{DP}) of polymers ranged between 18 and 70, as represented in Table I. This means that the products are mainly oligomers.

From Table I one can notice that conversion % of *VIa* and consequently of *VIb* under the basic conditions of method A is very low ($\sim 25\%$). This can be attributed to the formation of the low molecular weight cyclic product, piperazine, rather than formation of oligomeric product. Piperazine formation was confirmed through detection by TLC referred to an authentic sample using different compositions of the eluent system (ethyl acetate/light petroleum: 1 : 9, 2 : 8, and 3 : 7). Therefore, it can be concluded that a cyclization reaction competes, as expected, with that of oligomerization leading to lower conversion percent. It is important to mention that a low conversion was also observed with *IIIa* and consequently with *IIIb* ($\sim 40\%$) under the conditions of method A. Condensations of numerous alkylene dichlorides and alkylene polyamines carried out by Suen, Jen, and Moore¹¹ demonstrated the validity of the Carother's rule that high polymers will not result if the formation of 5- or 6-membered rings is possible.^{19,20}

Similar reactions were carried out using *m*- and *p*-phenylene diamine. The reaction of both diamines resulted in the formation of oligomers with higher conversion using both dichloroalkanes as alkylating agents. This is attributable

to the stereochemical suppression of the cyclization reaction. Also, oligomerization of ethylenediamine with both dichloroalkanes under the conditions of method B led to formation of oligomers with higher conversions than by method A. The aromatic diamines resulted in formation of oligomers with reasonable conversions close to each other and higher than of ethylenediamine.

Analysis

IR (*KBr*) versus (cm^{-1}): 2900 (CH—aliph.) and 700 (C—Cl stretch.) for all samples (*III-VIII*). 1510 (CH—aromatic) for samples *IV, V, VII, and VIII*. 1610 ($^+\text{NH}_2$), 1400 (C—N $^+$) and weak absorption at 1600 (^+NH) and 1500 ($^+\text{NH}_3$) for samples *IIIa-VIIIa*. $^1\text{H-NMR}$ (DMSO-*d*₆) δ (ppm): For samples *IVb* and *Vb* 6.8 multiplet (C₆H₄); 4.3 split singlet (CH₂) and 5.3 singlet (two NH). For samples *VIIb* and *VIIIb* 6.8 multiplet (C₆H₄); 2.8 triplet (C₂H₄NH); 4.1 triplet (C₂H₄Cl) i.e., centered at 3.4 (C₂H₄) and 5.3 singlet (two NH). For samples *IIIb* and *VIb* about 4.3 (aliphatic six protons of three CH₂ groups and eight protons of four CH₂ groups, respectively). The spectra were generally broad. Figure 1 illustrates the $^1\text{H-NMR}$ spectrum of the neutralized polymeric product *VIIb* as an example. Elemental analysis data are shown in Table II.

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