

# Synthesis and Application of Some Oligopolyamines as Adhesives for Road Bitumens

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**ABSTRACT:** By the amination of a fraction of *n*-polychloroparaffins (C<sub>13–19</sub>) with 1,2-ethylenediamine in a basic medium, oligopolyamines were obtained. The obtained products were characterized with spectroscopic, titrimetric, and elemental analyses and tested as adhesives for road bitumens. The samples, containing over 7.0% bound nitrogen in a concentration of 1.0 mass % with respect to the bi-

tumen mixtures, were characterized by maximum effectiveness, that is, 100% adhesion between the bitumen and the mineral fillers. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3300–3304, 2009

**Key words:** adhesives; oligomers; polyelectrolytes; synthesis; water-soluble polymers

## INTRODUCTION

Polyalkylene-polyamines have been previously synthesized through the reaction of aromatic amines with alcohols, and they require a pressure of 8.0 MPa and a temperature of 553 K.<sup>1</sup> Diamines such as ethylenediamine (EDA) can react with dihalides in a basic medium.<sup>2</sup> By the condensation of trialkylamines with halogen paraffins, polyamines have been obtained.<sup>3</sup> Noncyclic polyalkylene-polyamines were synthesized by Agrawal and Frey.<sup>4</sup> By the amination of a fraction of *n*-polychloroparaffins (PCPs) with EDA at pressures of 0.5–1.0 MPa and at temperatures of 423–473 K, highly aminated polyfunctional oligomers have been obtained and used as biocides after quaternization.<sup>5</sup> As cationic surface-active substances, these compounds have been found to be useful in many different applications.<sup>6–11</sup>

The experience with the use of asphalt-concrete coatings has shown that their destruction is mainly due to poor adhesion between the bitumen and the mineral fillers.<sup>12,13</sup> Different cation surface-active substances are effective for the improvement of cohesion. Alkyldiamines, alkylpolyamines, ethoxylated amino compounds, and so on, usually produced from natural and synthetic fatty acids, are useful mainly as adhesives.<sup>14,15</sup>

The first aim of this work was to study the synthesis of oligopolyamines on the basis of PCPs with EDA as an aminating agent. To avoid some lateral reactions such as cyclization, deamination, and cross-

linking, which are characteristic of the amination of dihalides with diamines in organic solvents, the syntheses were carried out under lower pressures and temperatures in an aqueous basic medium. The second aim of this work was to establish the possibility of using these amino compounds as adhesives for road bitumens.

## EXPERIMENTAL

All solvents were purified by the standard methods.<sup>16</sup> PCP represents a fraction chlorinated in 47% *n*-paraffin (with chlorine atoms at the end of the chain) with the following composition: C<sub>13</sub>, 10.3%; C<sub>14</sub>, 30.4%; C<sub>15</sub>, 26.1%; C<sub>16</sub>, 19.4%; C<sub>17</sub>, 10%; C<sub>18</sub>, 2.3%; and C<sub>19</sub>, 1.5%. This corresponded to a summary formula of C<sub>15</sub>H<sub>27</sub>Cl<sub>5</sub> with an average molecular weight of 385, a density (293 K) of 1210 kg/m<sup>3</sup>, and a viscosity (295 K) of 0.550 Pa s (AD Polychim, Devnya, Bulgaria). EDA was extra pure (Ferak). Hydrochloric acid and sodium hydroxide were pure for analysis (Merck, Darmstadt, Germany).

Elemental microdetermination was carried out with a Carlo-Erba model 1104 autoanalyzer. Fourier transform infrared spectroscopy analysis was carried out with a PerkinElmer model 1750 spectrophotometer in solution (with nuyol as the solvent). <sup>1</sup>H-NMR and distortionless enhancement by polarization transfer/nuclear magnetic resonance (DEPT-NMR) spectroscopy analysis was carried out in the solvent chloroform with a Bruker DRX 250-MHz <sup>1</sup>H-NMR spectrometer. The number-average molecular weight (*M<sub>n</sub>*) was determined by the isopiestic method (isothermic distillation) with the solvent chloroform.<sup>17</sup> The determination of nitrogen in the form of primary, secondary, and tertiary amino groups (I, II,

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TABLE I  
Chemical Compositions and  $M_n$  Values of the Samples in the Free Base Form Synthesized at 428 K over the Course of 2 h

No.	PCP/EDA molar ratio	C (%)	H (%)	N (%)	O (%)	Cl (%)	Amino group (%)			$M_n$
							I	II	III	
1	0.218	60.1	8.05	9.10	1.52	22.2	2.65	5.44	1.01	1850
2	0.265	57.44	8.01	8.72	1.53	24.3	2.10	5.22	1.32	2200
3	0.313	58.12	7.94	7.04	1.56	25.3	1.60	3.83	1.61	2530
4	0.358	58.00	7.82	6.33	1.65	26.1	2.10	5.22	1.76	2400
5	0.405	56.21	7.61	5.07	1.71	29.4	0.61	2.70	1.83	2100
6	0.452	55.80	7.41	4.03	1.76	31.0	0.30	1.86	1.87	1600
7	0.498	55.97	7.32	3.65	1.82	35.2	0.24	1.40	2.03	1510

and III) was performed by the acidimetric method for separate amine titration.<sup>18</sup> The viscosity was determined by the method of Stox.<sup>19</sup>

The coefficient of atmospheric resistance and adhesion between the bitumen and the mineral filler were determined by standard methods<sup>12</sup> for a structure containing bitumen B 60/90 as a binding agent, different activating additives, and a 5/15-mm fraction of the acid mineral filler.

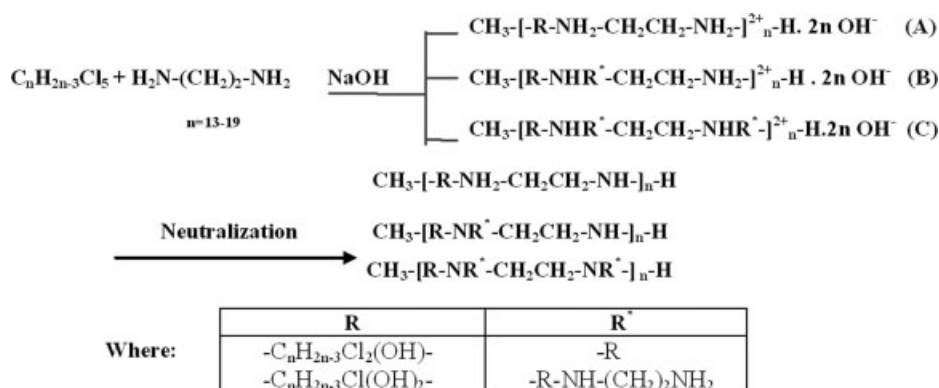
### Synthesis

A stainless steel autoclave, supplied with a shaker and a straight cooler, was charged with 0.26 mol of PCP (100.1 g), a 50% water solution of EDA (in different amounts according Table I), and 0.45 mol (18 g) of sodium alkali, which was used as a basic catalyst in the form of a 40% water solution. It was added in an amount equivalent to the bound chlorine in PCP. The autoclave was heated with steam fed into the apparatus jacket and cooled with water when it was necessary. Dependent on the temperature, the autoclave pressure increased from 0.1 to 0.5 MPa. A number of products were synthesized with different technological parameters: temperatures of 393–433 K and different reaction times. At 428 K with a reaction time of 2 h, the influence of

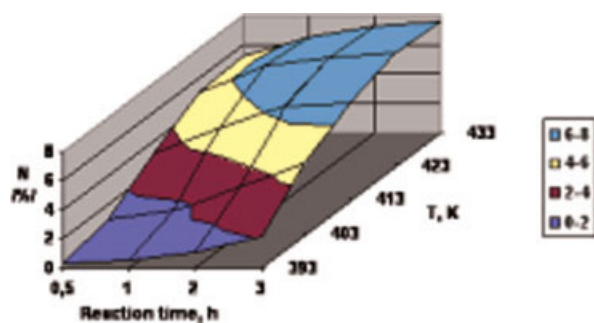
the PCP/EDA molar ratio on the chemical composition and  $M_n$ , as well as the rate of conversion (RC) of the initial PCP to polyamines, was investigated. After the synthesis was complete, the nonreacted EDA was distilled at 388–423 K. The reaction mixture was cooled, diluted with diethyl ether with a 1 : 1 ratio of the solvent to the product, and left for 1 h for the precipitation of the solid sodium chloride phase. The solvent (diethyl ether) was evaporated, and the organic phase was left for 8 h for separation of the nonreacted PCP, which, being heavier, settled at the bottom. After the separation of PCP, the residue was dried for 4 h at 378 K and investigated to determine its chemical composition and properties as an adhesive for a Bulgarian mark of road bitumen.

### RESULTS AND DISCUSSION

This work was aimed at the synthesis of oligopolyamines under weaker conditions (low pressures of 0.1–0.5 MPa and low temperatures), their characterization, and their testing as adhesives for road bitumens. By the amination of PCP with EDA in the presence of a basic catalyst such as a 40% water solution of sodium alkali, oligomeric products were obtained in a —OH form. They were converted into a free base form by neutralization with hydrochloric



Scheme 1 Reaction equations for the synthesis of polyamines under the conditions shown in Table I.



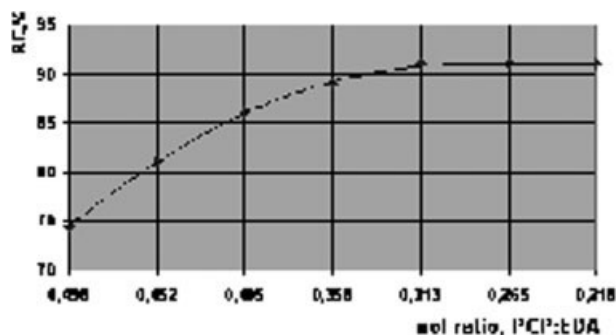
**Figure 1** Dependence of the content of bound nitrogen on the reaction time and temperature with a PCP/EDA molar ratio of 0.313. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

acid (Scheme 1). The process of amination was exothermal and proceeded at a high temperature over 393 K (Fig. 1). Dependent on the temperature, the autoclave pressure was changed from 0.1 to 0.5 MPa. The content of bound nitrogen (N) increased, being dependent on the temperature and reaction time, and reached its highest values at 423–433 K with reaction times of 2–3 h. The samples synthesized at 428 K for 2 h, with different molar ratios of PCP to EDA, were analyzed for their C, H, N, and O contents, residual chlorine, types of amino groups, and  $M_n$  values (Table I). RC of PCP to polyamine with different PCP/EDA molar ratios is shown in Figure 2. It increased to a molar ratio of 0.313 when  $M_n$  reached its highest value. This could be explained with the equivalent ratio of EDA to active chlorine atoms in PCP.

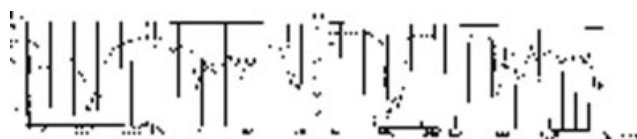
### Characterization

All obtained products were brown-red liquids that were quite water-soluble in hydrochloric and hydroxide forms with a density of 1080–1100 kg/m<sup>3</sup> and a viscosity (295 K) of 0.617–0.630 Pa s.

Figure 3 illustrates the IR spectrum of sample 3 (Table I) in a free base form. Fourier transform infra-



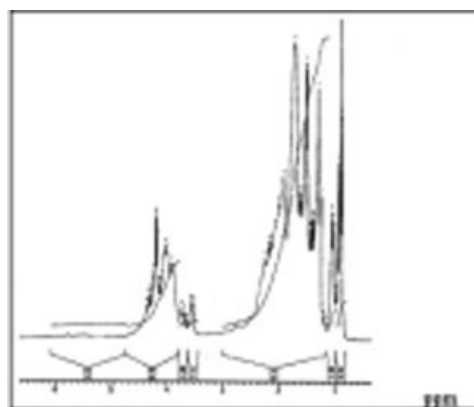
**Figure 2** RC of PCP with different molar ratios of PCP to EDA.



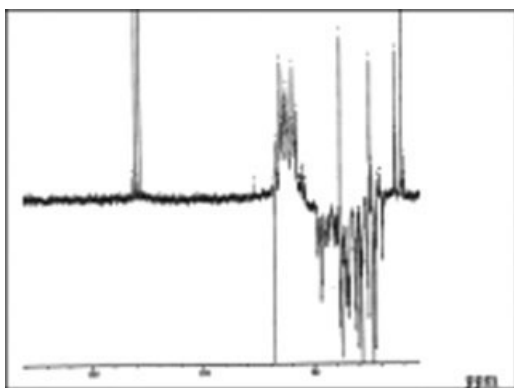
**Figure 3** IR spectra of sample 3 in the free base form and the initial PCP.

red spectroscopy analysis showed absorptions at 2861 and 680 cm<sup>-1</sup> corresponding to aliphatic CH— and C—Cl stretching, respectively, for all samples.<sup>20</sup> For samples corresponding to formulas A, B, and C (Scheme 1), absorptions at 1610 and 1400 cm<sup>-1</sup>, corresponding to NH<sub>2</sub><sup>+</sup> and CN<sup>+</sup>, respectively, indicate the presence of oligomers in the OH form. The absorptions at 1590 and 1500 cm<sup>-1</sup>, corresponding to NH<sup>+</sup> and NH<sub>3</sub><sup>+</sup>, indicate the presence of branching due to double-alkylated amine centers. Absorptions at 1059 and 1126 cm<sup>-1</sup> are due to the presence of OH groups at the end and OH groups along the oligomeric chain. The absorption at 3350 cm<sup>-1</sup> corresponds to NH and NH<sub>2</sub> groups. The absence of an absorption at 1400 cm<sup>-1</sup>, corresponding to CN<sup>+</sup> indicates that samples 1–7, corresponding to formulas A<sub>1</sub>, B<sub>1</sub>, and C<sub>1</sub>, were completely free of amine-hydroxide centers. For comparison, the IR spectrum (nuyol) of the initial PCP on the right is shown, containing absorptions corresponding only to aliphatic CH— and C—Cl stretching. The absorption at 3350 cm<sup>-1</sup>, corresponding to NH and NH<sub>2</sub> groups, is missing. The absorption at 1126 cm<sup>-1</sup>, corresponding to the presence of OH groups, is an indication that the initial PCP must have been partially hydrolyzed.

The <sup>1</sup>H-NMR spectrum of sample 3 (Table I), with peaks from 0.89 to 1.1 ppm, shows long alkyl chain —CH<sub>2</sub>— and —CH<sub>2</sub>— toward CH<sub>3</sub>. Peaks from 1.25 to 1.75 ppm correspond to —CH<sub>2</sub>— toward polar substitutes. —CH<sub>2</sub>— toward secondary and tertiary amino groups can be observed in the arm of 1.75–



**Figure 4** Adhesion of the asphalt mixture with different amounts of bound nitrogen in the adhesives.

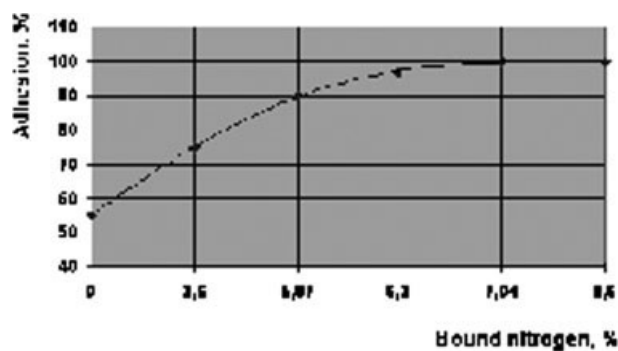


**Figure 5**  $^1\text{H-NMR}$  spectrum of sample 3 in the free base form (Table I).

2.25 ppm. Peaks from 3.5 to 3.8 ppm correspond to  $-\text{CH}_2-$  toward the OH group and  $\text{Cl}-$ . Peaks in the range of 3.8–4.2 ppm correspond to CH groups in the  $\alpha$  position toward Cl. Peaks at 5.46 ppm correspond to a double bunch toward  $-\text{CH}_2$  (Fig. 4).

The DEPT-NMR spectrum of sample 3 in Table I (Fig. 5) gives more exact information about the structure of the polyamines. Peaks corresponding to  $-\text{CH}_2-$  are shown in the range of 10–14 ppm. Peaks at 24–25 ppm probably correspond to a CH bond along the oligomeric chain. C atoms next to Cl and OH— groups show peaks at 38.5 ppm and in the range of 57–66 ppm, which depend on the neighboring group and  $\alpha$  and  $\beta$  positions. Peaks at 127–132 ppm probably correspond to double  $\text{C}=\text{C}$  stretching. As expected,  $-\text{CH}_2-$  C atoms in this complicated system can be observed in the range of 20–40 ppm. This range is large because of the multifunctional system.

The double-alkylated amine centers are an indication of branching or crosslinking of the chains. According to Prodanov,<sup>5</sup> in this reaction system of PCP–diamines in a basic medium, crosslinking, connected to resin formation, proceeds mainly at a temperature higher than 433 K by a deficit of the aminating agent in the reaction mixture (lower than the equivalent amount) and longer reaction times (6–10 h). The products obtained under these conditions have lower water solubility. To avoid lateral reac-



**Figure 6** DEPT-NMR spectrum of sample 3 (Table I) in the free base form.

tions such as crosslinking and cyclization, which are typical for the interaction of low-molecular-weight diamines and dihalides in the presence of solvents,<sup>2,19,21</sup> the condensation was carried out without an organic solvent, with long-chained PCP, at 428 K for a reaction time of 2 h. All the samples had a low viscosity, and the gel fraction was missing. This indicated an absence of crosslinked oligomers.<sup>19,22</sup>

Therefore,  $M_n$  can be calculated according to the formula  $\text{CH}_3-[-\text{R}-\text{NR}^*-\text{CH}_2-\text{CH}_2-\text{NH}-]_n-\text{R}^*$ , where  $\text{R}^*$  (Scheme 1) can be H, R, or  $\text{R}-\text{NH}-(\text{CH}_2)_2\text{NH}_2$ .

It can be concluded that according to samples 1–4 (Table I), formula A is insignificantly dominant. Formula B is dominant with less EDA in the reaction mixture (PCP/EDA molar ratio  $> 0.358$ ), corresponding to samples 5–7. According to sample 7 and partially sample 6, the ratio of II/III amino groups indicates that both amine centers are double-alkylated (formula C).

## Application

To be a good and economically advantageous adhesive for bitumens, one compound should ensure 100% adhesion with a concentration of 1.0 mass %. Adhesives were incorporated into bitumen at 1.0 mass %. A dominating influence on the adhesion effect was exerted by the bound nitrogen content in the samples.<sup>6,8</sup> A comparison of the adhesion effectiveness of the samples containing different

**TABLE II**  
Atmospheric Resistance of the Asphalt Mixtures Produced with Rocky Material and Adhesives Containing Different Amounts of Bound Nitrogen

No.	Kind of binding material in the asphalt mixture	Content of nitrogen (%)	Atmospheric resistance (%)
1	Bitumen Bulgaria 60/90, Bulgaria	—	0.51
2	Bitumen Bulgaria 60/90, Bulgaria + 1.0% adhesive	5.07	0.69
3	Bitumen Bulgaria 60/90, Bulgaria + 1.0% adhesive	6.33	0.80
4	Bitumen Bulgaria 60/90, Bulgaria + 1.0% adhesive	7.04	0.86
5	Bitumen Bulgaria 60/90, Bulgaria + 1.0% adhesive	9.10	0.87



amounts of bound nitrogen is presented in Figure 6. The correlation between the content of primary amino groups in the samples and the adhesive effectiveness is most expressed by the formation of a more stable membrane on the bitumen–mineral filler border surface with a greater content of primary amino groups.<sup>8</sup> The data for the atmospheric resistance of asphalt mixtures produced with a rocky material and adhesives containing different amounts of bound nitrogen, after 2 years of exploitation, are shown in Table II. The experimental results show that the atmospheric resistance in the presence of the adhesive increased from 0.69 to 0.87% according to the percentage of bound nitrogen in the samples in comparison with sample 1 without an adhesive, which had a much lower atmospheric resistance of 0.51%.

### CONCLUSIONS

A possibility for producing oligopolyamines by the amination of PCP with EDA in the presence of sodium alkali, under conditions that do not permit crosslinking, which is related to resin formation, has been reported. These compounds can successfully be applied as adhesives for road bitumens in cases of unsatisfactory adhesion between the bitumen and mineral fillers. The adhesive effectiveness depends only on the amount of bound nitrogen and especially on the content of primary amino groups. Adhesives containing 7.0 mass % or more bound nitrogen at a concentration of 1.0 mass % against the bitumen mixtures were characterized by maximum effectiveness.

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