

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### The Amination Kinetics of Bromomethylated poly(2,6-Dimethyl-1,4-Phenylene Oxide) with Diethylamine

Juraj Líška<sup>a</sup>; Eberhard Borsig<sup>a</sup>

<sup>a</sup> Polymer Institute Slovak Academy of Sciences, Bratislava, Slovak Republic

**To cite this Article** Líška, Juraj and Borsig, Eberhard(1994) 'The Amination Kinetics of Bromomethylated poly(2,6-Dimethyl-1,4-Phenylene Oxide) with Diethylamine', *Journal of Macromolecular Science, Part A*, 31: 12, 2019 – 2031

**To link to this Article:** DOI: 10.1080/10601329409350116

**URL:** <http://dx.doi.org/10.1080/10601329409350116>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# THE AMINATION KINETICS OF BROMOMETHYLATED POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE) WITH DIETHYLAMINE

JURAJ LÍŠKA and EBERHARD BORSIG

Polymer Institute  
Slovak Academy of Sciences  
Dúbravská cesta 9, 842 36 Bratislava, Slovak Republic

## ABSTRACT

We have studied the influence of temperature, the type of solvent, and concentration of reagents on the kinetics of amination reaction of a bromomethyl derivative of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with diethylamine. The amination reaction was found to follow a second-order rate law. The rate of reaction decreases together with decreasing polarity of the reaction medium. At high temperatures (80 and 100°C), or if the mixture becomes thicker by removal of the solvent, we observed crosslinking of the polymer caused by reaction of unreacted bromomethyl groups of PPO with already bound diethylamine groups to the neighboring polymer chains with the formation of an ammonium salt. The gel portion grows with increasing temperature and with the concentration of polymer in the reaction mixture.

## INTRODUCTION

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is rarely used alone for commercial purposes. Its processing is rather difficult, and therefore it is frequently applied only in mixture with other polymers with good miscibility, usually polystyrene [1–3]. PPO is not miscible with polar polymers. One of the ways to increase

PPO miscibility with polar polymers is by chemical binding of polar groups to PPO chains [4–7].

In this work we have chosen the amino group as a polar group for binding to PPO. Since the PPO chain does not contain any typical reactive groups that would provide possibilities for direct binding of functional groups with high reaction conversion, we have used a procedure based on the preparation of the bromomethyl derivative of PPO. The bromomethyl derivative is a generally efficient precursor for consequent nucleophilic substitution reactions with different nucleophiles; in this case we expected it would work the same way with diethylamine. Our study of this reaction has aimed at obtaining basic data about the kinetics and the efficiency of the condensation reaction of the bromomethyl derivative of PPO with diethylamine.

Analogous to the considered amination reaction of the bromomethyl derivative of PPO are reactions of the chloromethyl derivative of polystyrene with amines which follow second-order kinetics. Amination of the chloromethyl derivative of polystyrene with primary and secondary amines progresses in two stages. In the second stage, the reaction slows down. The reaction of the chloromethyl derivatives of polystyrene with tertiary amines follows second-order kinetics without any deviation observed in the kinetics of the process [8–11]. On the other hand, an influence of the polymer medium on the condensation reaction of the bromomethyl derivative of PPO and diethylamine and on the course of secondary reactions was expected.

## EXPERIMENTAL MATERIALS

PPO (Nerafene, a product of Spolana Neratovice) [ $\eta$ ] = 0.5 dL/g (chloroform, 25°C),  $M_n$  = 21,000 (determined by vapor-phase osmometry). The polymer was purified by precipitation from its chloroform solution into methanol and dried in a vacuum drier. Liquid bromide, dicumyl peroxide, chlorobenzene, methanol, diethylamine, and triethylamine (all of analytical purity from Lachema) were used as received.

## PROCEDURE

### Bromomethylation of PPO

The general procedure utilized for the preparation of bromomethylated PPO, described elsewhere [4], was as follows. One gram purified PPO was dissolved in 135 mL chlorobenzene in a 250-mL four-necked flask equipped with a mechanical stirrer, thermometer, condenser, and nitrogen inlet, and heated to the reflux temperature (132°C) of chlorobenzene. Then a solution of 0.2 g dicumyl peroxide in 8 mL chlorobenzene was added dropwise, as well as a solution of a required amount of molecular bromine in 36.6 mL chlorobenzene. The reaction mixture was kept at the reflux temperature of the solvent for 2 hours. The brominated polymer was precipitated from the warm solution washed with methanol, and dried under vacuum at 80°C for 12 hours. The applied reaction conditions were such that the bromination proceeded exclusively on the methyl groups of PPO [12]. The volume of bromine was determined by elementary analysis, and  $^1\text{H-NMR}$  spectroscopy

showed that there were chemical shifts of methyl protons (2.03 p.p.m.) and methylene protons (4.26 p.p.m.) but no shifts for phenyl protons of substituted units of PPO. These values are in agreement with our previous results [12]. This procedure resulted in samples with bromine contents of 6.5, 11, 21, 31, and 40 mass%; that is, 16, 28, 52, 77, and 97 mol% PPO units with one bound bromomethyl group.

### Preparation of Diethylamino Derivative of PPO

Kinetic measurements of the condensation reaction were carried out in equipment consisting of a 500-mL round-bottom flask with a stirrer and a cooler. It was heated in an oil bath. Three grams of the corresponding bromomethyl derivate of PPO was dissolved in 297 g of the solvent (chloroform, chlorobenzene, or toluene). The solution was heated to the reaction temperature, and diethylamine was added. Samples of the reaction mixture were removed from the reaction flask at defined time intervals. The polymer was precipitated with a 10× methanol overdose. The precipitated polymer product was washed with methanol, dried in a vacuum drier at 80°C at  $p = 0.05$  torr for 12 hours. Reactions at temperatures above the boiling point of diethylamine (56°C) were carried out in sealed ampules.

Elementary analysis was used to determine the ratio of bromine and nitrogen. Reactions with triethylamine were carried out in a similar way. The portion of gel in the samples was determined as the insoluble part of the polymer product of the amination reaction of bromomethylated PPO. Approximately 3 g of polymer product was extracted twice in fresh chloroform under reflux for half an hour, and the insoluble residue was washed with pure chloroform and dried as described above.

## RESULTS AND DISCUSSION

We expected the reaction of bromomethyl derivatives of PPO with diethylamine to be controlled by second-order kinetics, analogous to the cases of chloromethyl derivatives of polystyrene with primary, secondary, and tertiary amines [9–11]. In general, the kinetics of a bimolecular reaction controlled by second-order kinetics ( $S_N2$  mechanism) can be expressed by a rate equation [1]:

$$v = dx/dt = k(a - x)(b - x) \quad (1)$$

which, by integration, leads to Eq. (2):

$$k = \frac{2.303}{(a - b)t} \log \frac{1 - \alpha}{1 - \beta} \quad (2)$$

where  $v$  is the reaction rate;  $k$  is the rate constant;  $t$  is the time;  $a$  and  $b$  are the starting concentrations of diethylamine and bromine, respectively;  $\alpha$  and  $\beta$  are the ratios  $x/a$  and  $x/b$ , where  $x$  is the concentration of reacted amino groups in time  $t$ , expressed as the bromine content in the sample at the reaction time. The logarithmic dependencies of conversion of the condensation reaction of the bromomethyl derivative of PPO with diethylamine on time at different temperatures (20, 30, and 50°C) are shown in Fig. 1. In fact, they are graphical solutions of Eq. (2) where the linear dependence gradient allows calculation of the rate constant. Similar logarithmic

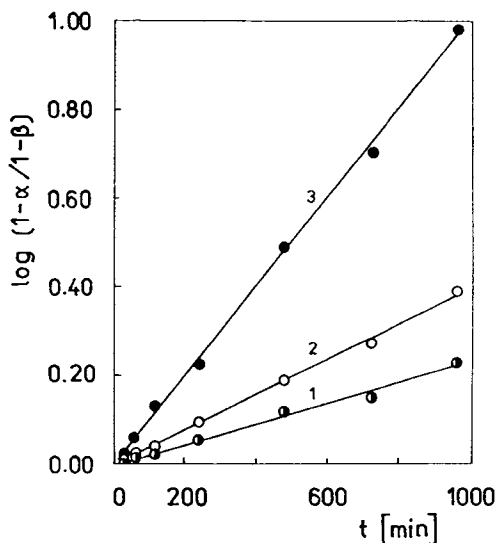


FIG. 1. Conversion curves of amination of the bromomethyl derivative of PPO (21 mass% Br) by diethylamine in a solution of chlorobenzene at 20 (1), 30 (2), and 50°C (3), expressed by a kinetic equation of the second order (1 mass% of the polymer in the solution, the molar ratio of diethylamine/bromine = 5:1).

mic dependencies on time were observed in condensation reactions carried out under the same concentration conditions in chloroform (Fig. 2). The reaction rate was much higher as indicated by the increased values of the rate constants when the reaction was carried out in chloroform (Table 1). The straight-line dependencies in Figs. 1 and 2 suggest that the condensation reaction of the bromomethyl derivative of PPO with diethylamine is controlled by kinetics of the second order.

Under the same reaction conditions with the toluene solution, we observed a similar course of conversion dependence of the condensation reaction but with considerably lower rate than for chlorobenzene and chloroform (Fig. 3 and Table 1). At a certain stage of conversion, the reaction slows down, as shown by the bends in Fig. 3. This can be explained by a decrease of polymer solubility after a certain stage of conversion. Since increasing the portion of amino groups in the chain makes it more polar, in a nonpolar medium the polymer coil wraps more tightly and becomes less accessible for bromomethyl groups. This phenomenon is accompanied by polymer precipitation from the solution as observed in our experiments by the increasing turbidity of the solution. If the condensation reaction under the same reaction conditions in toluene (at 50°C) uses bromomethyl derivatives with an increased portion of bromomethyl groups, the dependence bend occurs much earlier, and the reaction rate decrease is much more significant. This supports the above idea that the reaction rate decrease is caused by lower polymer solubility under the influence of an increasing portion of the amine groups being bound to the polymer chain. From the dependence before and after the bend in Fig. 4, we have calculated reaction rate constants (Table 1) for the case when toluene is used as the solvent.

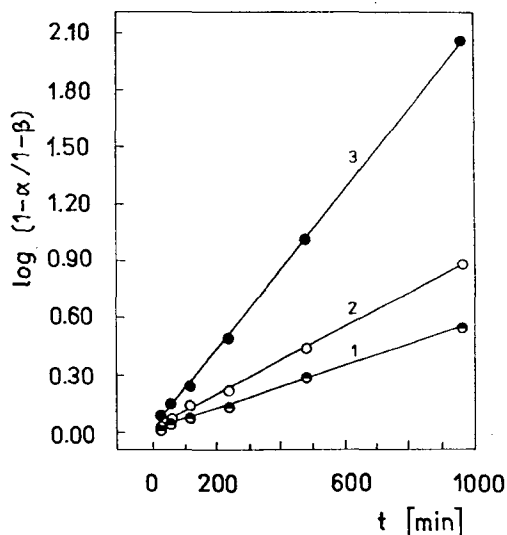


FIG. 2. Conversion curves of amination of the bromomethyl derivative of PPO (21 mass% Br) by diethylamine in a solution of chloroform at 20 (1), 30 (2), and 50°C (3), expressed by a kinetic equation of the second order (1 mass% of polymer in the solution, the molar ratio of diethylamine/bromine = 5:1).

We have calculated the corresponding activation energies and preexponential factors for the reactions in all the above-mentioned solvents from the dependence of the rate constant on the temperature. The results graphically calculated (Fig. 5) according to the Arrhenius equation in logarithmic form (Eq. 3) are in Table 1.

$$\log k = \log A - 2.303RT \quad (3)$$

TABLE 1. Kinetic Parameters of Amination of the Bromomethyl Derivative of PPO (21 mass% Br) with Diethylamine in Different Solvents at 20, 30, and 50°C<sup>a</sup>

Solvent	$\epsilon$	$\mu$	$k, (\text{L/mol}\cdot\text{s}) \times 10^4$			$A, (\text{L/mol}\cdot\text{s}) \times 10^{-3}$	$E, \text{kJ/mol}$
			20°C	30°C	50°C		
Toluene <sup>b</sup>	2.391	0.36	$a_1$ : 1.200	2.160	6.00	3.20	41.6
			$a_2$ : 0.028	0.53	0.17	0.73	47.2
Chlorobenzene	5.708	1.69	11.000	17.000	46.00	8.30	38.7
Chloroform	4.806	1.01	25.000	41.000	99.00	7.1	36.2

<sup>a</sup> $\epsilon$  = dielectric constant of the solvent;  $\mu$  = dipole moment;  $k$  = rate constant;  $A$  = preexponential factor;  $E$  = activation energy.

<sup>b</sup>In the case of toluene the reaction has two stages with different  $k$ ,  $A$ , and  $E$  values. The data in line  $a_1$  are calculated from the dependencies in Fig. 3 before the bend and those in  $a_2$  from the dependencies after the bend.

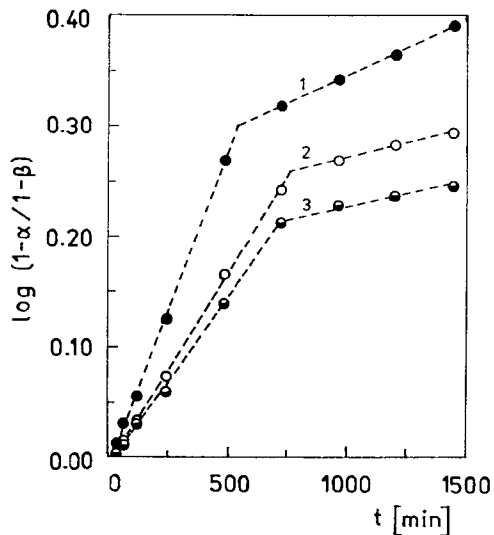


FIG. 3. The values of amination conversion of the bromomethyl derivative of PPO (21 mass% Br) by diethylamine in a solution of toluene at 20 (1), 30 (2), and 50°C (3), expressed by a kinetic equation of the second order.

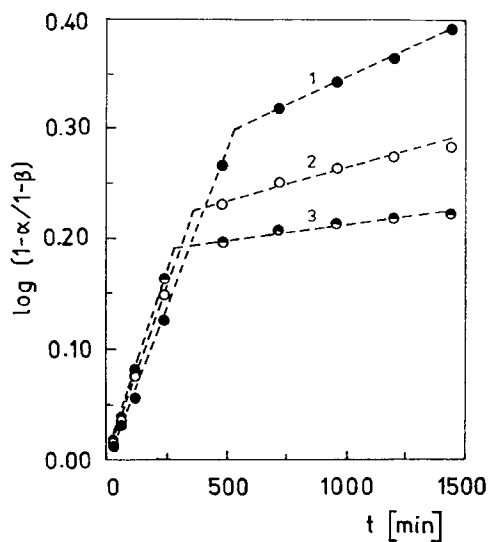


FIG. 4. The values of the reaction conversion of the bromomethyl derivative of PPO with the a mass% Br content of 21 (1), 31 (2), and 40 (3) by diethylamine in a solution of toluene at 50°C, expressed by a kinetic equation of the second order.

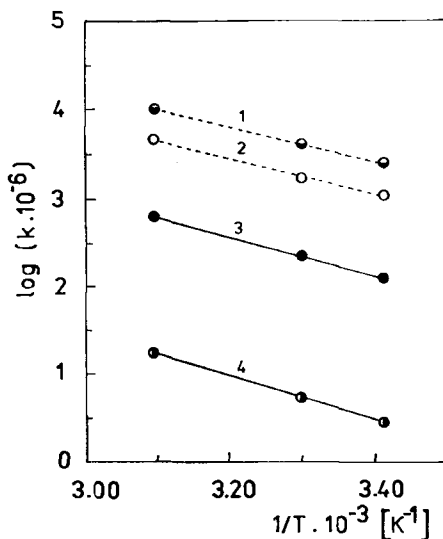


FIG. 5. The dependence of the amination rate constant of the bromomethyl derivative of PPO (21 mass% Br) by diethylamine in solutions of chloroform (1), chlorobenzene (2), toluene (3) [at the higher reaction rate before the "bend"] and toluene (4) [after the "bend"]. See Fig. 3.

We can make several assumptions from Table 1. The reaction rate constant grows with increasing polarity of the reaction medium and the temperature. The lowest activation energy and the highest preexponential factor are observed for reaction in chloroform despite the fact that chloroform has a lower dielectric constant and a lower dipole moment than chlorobenzene. Comparison of the condensation reaction in all three solutions (toluene, chlorobenzene, and chloroform) leads us to conclude that good solubility of the original polymer and the reaction product is not the only requirement for a solvent. There is also need for a good ability to transport the reagent to the place of reaction in the polymer chain. The polymer reaction site in the polymer chain ( $-\text{CH}_2\text{Br}$  group) and the one in the reagent itself (diethylamine) have two different dielectric constants. Therefore the chosen solvent has to interact with the two reagents as well as possible. Our observations suggest that chloroform is the closest to meeting the required qualities of the three solvents.

When the condensation reaction of the bromomethyl derivative of PPO (21 mass% Br) with diethylamine in a solution of chlorobenzene took place at high temperatures (80 and 100°C) we observed an increased speed of reaction in the first stage compared to reaction at 50°C (see Figs. 1 and 6). After a certain stage of conversion, the reaction rate decreased (Table 2) and the solution became cloudy. The cloudiness is caused by the formation of gel which was determined in the reaction product. On the other hand, elementary analysis shows a higher volume of residue bromine in the polymer after the reaction is completed compared to the reaction under the same conditions at 50°C (Table 3). We conclude that if the condensation reaction takes place at high temperatures, a reaction of bound diethyl-



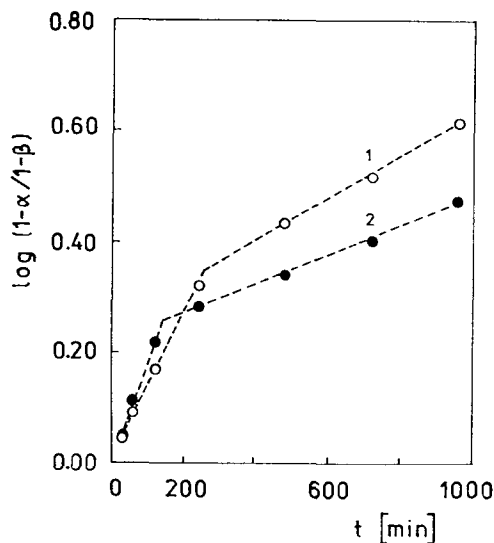
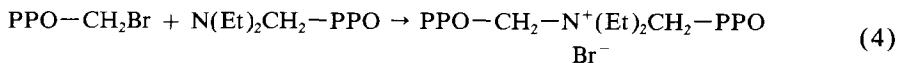


FIG. 6. The values of amination conversion of the bromomethyl derivative of PPO (21 mass% Br) by diethylamine in a solution of chlorobenzene at 80 (1) and 100°C (2).

amino groups with unreacted bromomethyl groups produces ammonium salt. That leads to crosslinking of the polymer:



The increased volume of bromine in the product of the high-temperature condensation reaction implies that the formation of ammonium salt happens at the expense of the amination reaction. The formation of ammonium salt as a side product of the condensation reaction of the bromomethyl derivative of PPO with

TABLE 2. Kinetic Parameters of the Course of Amination of the Bromomethyl Derivative (21 mass% of Br) with Diethyl- and Triethylamine in Chlorobenzene Solution. Temperature Scale: 50–100°C.

Reaction temperature, °C	Diethylamine		Triethylamine		<i>E</i> , kJ/mol
	<i>k</i> × 10 <sup>4</sup> L/mol·s				
	Before bend	After bend	Without bend		
50	46.0	—	4.4		
70	—	—	12.1		
80	64.2	40.9	—		46.7
100	72.6	32.0	45.3		

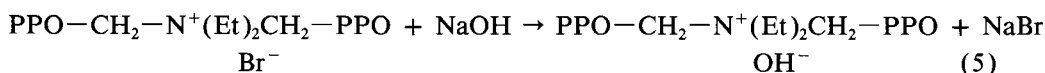
<sup>a</sup>*k* = rate constant of amination reaction; *E* = activation energy.

TABLE 3. The Mass% of Bromine in PPO after the Reaction of the Bromomethyl Derivative (21 mass% Br) with Diethylamine in Chlorobenzene Solution at Different Temperatures (reaction time = 8 hours)

Reaction temperature, °C:	20	30	50	80	100	80 <sup>a</sup>	100 <sup>a</sup>
Bromine content after extraction, wt%:	15.4	12.5	5.9	6.7	8.5	4.7	4.1

<sup>a</sup>After 8 hours extraction in the toluene-10% ethanolic mixture solution of NaOH at 80°C.

diethylamines is proven by the fact that after extraction of polymer following reaction in a mixture of toluene/10% alcohol solution of NaOH (1:1) at the boiling point, we found a smaller amount of bromine compared to before the extraction (Table 3) as a result of a change of an anion of Br for one of hydroxyl:



Similarly, we found that condensation of partially aminated samples of the bromomethyl derivative caused crosslinking. To provide that the ammonium salt is being created, we performed the following experiment: The bromomethyl derivative of PPO (21 mass% Br) reacted with diethylamine in chlorobenzene (temperature, 50°C) up to a conversion of 47% bromine. From the partly aminated samples we separated other reaction agents and prepared solutions in chlorobenzene with a polymer content of 1-10 mass%. The solutions were reacted at 80 and 100°C. We determined that the proportion of gel depends on the temperature and on the concentration of polymer in solution. We observed an increase in the cloudiness of the solution as well as an increase in the gel content of the reaction product (Table 4). The received data connote that with increases in the temperature and polymer concentration in the solution, the amount of gel in the sample also increases. Considering the fact that the content of nitrogen and bromine in the sample has not changed, we assume that formation of an insoluble gel is caused by ammonium salt according to Reaction (4) which creates crosslinks between polymer chains. Table 4 proves that at temperatures of 80 to 100°C, the reaction conditions are sufficient for formation of an ammonium salt between the bromomethyl groups of PPO and bound diethylamino groups. This reaction occurs in parallel with the diethylamine reaction with bromomethyl groups of PPO.

The formation of an ammonium salt in the partially aminated bromomethyl derivative of PPO is a reaction of two functional groups bound to the polymer chains. Therefore, we can expect that the polymer chain will influence the kinetics of this reaction. There is a model in which a part of the reaction forms macromolecules and the other part forms low molecular compounds: a reaction of the bromomethyl derivative of PPO with triethylamine. We followed the course of reaction of the bromomethyl derivative of PPO (21 mass% of Br) in a 1 mass% solution of chlorobenzene with triethylamine in a molar ratio of triethylamine and bromine of 5:1 at 50, 70, and 100°C:

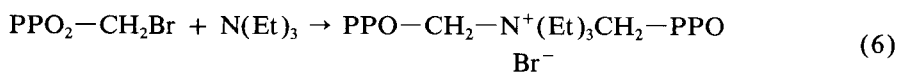


TABLE 4. The Amount of Gel Formed in the Interaction of Amino Groups with Bromomethyl Groups in Partially Aminated Samples of the Bromomethyl Derivative of PPO (24 mol% PPO units with the diethylamino group) in Chlorobenzene Solution at 80 and 100°C

Reaction temperature, °C:	Gel, mass%			
	80		100	
Polymer content, mass%:	1	10	1	10
Reaction time, h				
1	0	0	3	9
2	0	5	9	27
4	4	13	18	48
8	19	37	36	66
12	22	53	43	79

The conversion of Reaction (6) was determined with the help of the nitrogen content in the polymer.

It was found that Reaction (6) follows a second-order rate law (Fig. 7). As in the case of amination with diethylamine, the rate constants for the corresponding temperatures were calculated by the use of Relation (2). By using the Arrhenius equation, the activation energy and the preexponential factor of the reaction were

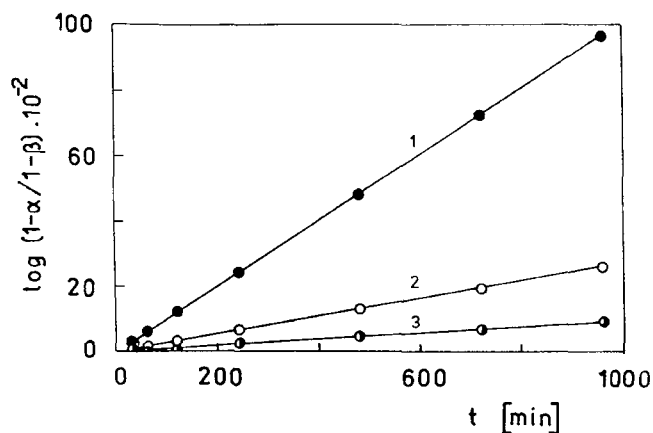


FIG. 7. The values of amination conversion of the bromoethyl derivative of PPO (21 mass% Br) by triethylamine in chlorobenzene solution at 100 (1), 70 (2), and 50°C (3), expressed by a kinetic equation of the second order.

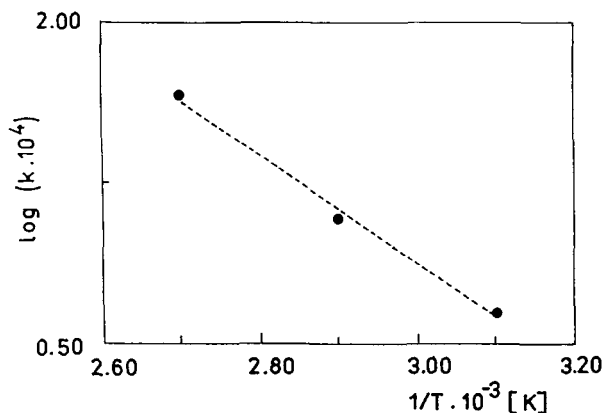


FIG. 8. The dependence of the rate constant of the amination reaction of the bromomethyl derivative of PPO (21 mass% Br) by triethylamine on temperature in a chlorobenzene solution.

calculated (Fig. 8 and Table 2). The values of the rate constants (Table 2) indicate that the rate of formation of the ammonium salt by reaction of the bromomethyl derivative of PPO and triethylamine is lower than amination by diethylamine under similar conditions. For steric reasons we generally expect that the formation of the ammonium salt will be slower than the amination reaction when diethylamine is used. This is proven by the increased activation energy with triethylamine (46.7 kJ/mol) over diethylamine (38.7 kJ/mol). Yet, if we compare the rate of formation of the ammonium salt in the two cases after chlorobenzene is used at 100°C (Table 2), we can see that the rate is higher in the first case. The slowing down of the reaction is due to the existing polymer network which makes the diffusion of more diethyl-

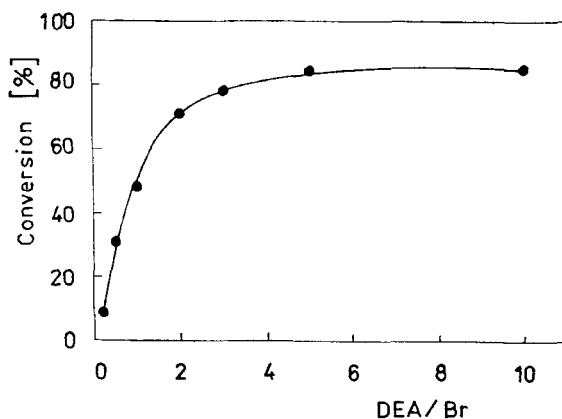


FIG. 9. The amination conversion curve of the bromomethyl derivative of PPO (21 mass% Br) with diethylamine in chlorobenzene solution at 50°C, and its dependence on the molar ratio of diethylamine (DEA) to bound bromine in PPO (reaction time = 8 hours).

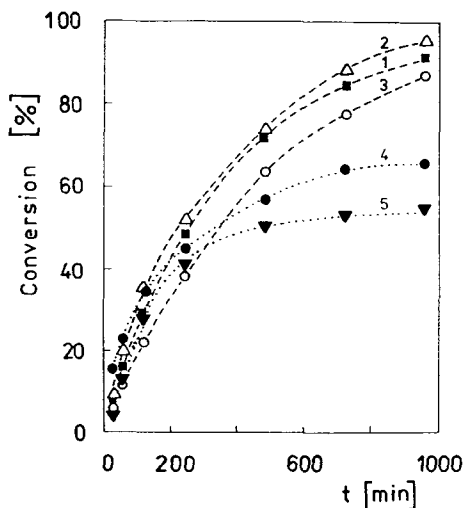


FIG. 10. Conversion curves of the diethylamine reaction with the bromoethyl derivative of PPO. Bromine content: 6.5 (1), 11 (2), 21 (3), 31 (4), and 40 (5) mass% in chlorobenzene solution at 50°C.

amine to the bromomethyl groups difficult. We think that the bends in the dependency curves (Figs. 3 and 6) actually characterize the crosslinking of the polymer and the transition to a diffusion controlled process of the condensation reaction.

In order to reach the highest possible yield of the amination reaction of the bromomethyl derivative of PPO with diethylamine, we followed the influence of the concentration of both reagents on reaction conversion in chlorobenzene at 50°C (Figs. 9 and 10). Figure 9 shows that 80% conversion is reached at a PEA/Br molar ratio of 3:1, and that any further increase of DEA does not change the conversion. At different bromomethyl group contents in the polymer, the increase of conversion over time is approximately 30% of the conversion for all samples (6.5, 11, 21, 31, and 40 mass% Br). Therefore, the increase of conversion by a higher content of bromomethyl groups in PPO (31 and 40 mass% Br) is significantly lower, probably due to polymer crosslinking. PPO with a higher bromomethyl group content will naturally be more inclined to crosslink, and the reaction will take place sooner than in the case of PPO with a lower bromomethyl group content (Fig. 10).

## CONCLUSIONS

Our kinetic study of the amination of the bromomethyl derivative of PPO with diethylamine and triethylamine indicates that the course of the condensation reaction follows a second-order rate law, but there are several deviations observed, mainly caused by formation of polymer networks by side reactions of ammonium salts. The rate of the amination reaction decreases with decreasing polarity of the environment in the series chloroform, chlorobenzene, toluene (where precipitation takes place even at low reaction conversions). At higher reaction temperatures (80

and 100°C) or when using PPO with a high content of bromomethyl groups (31 and 40 mass%), formation of ammonium salts was followed by mutual reaction of nonreacted bromomethyl and bound diethylamino groups. At a molar ratio of diethylamine to bromomethyl groups of 3:1 (their content equaled 21 mass% in the polymer), the conversion was 80%.

## REFERENCES

- [1] A. Davis, G. H. Deane, D. Gordon, G. V. Howell, and K. J. Ledbury, *J. Appl. Polym. Sci.*, **20**, 1165 (1976).
- [2] R. B. Seymour, *Polym. News*, **8**, 86 (1982).
- [3] U. Vogtländer, *Kunststoffe*, **33**, 9 (1982).
- [4] S. Percec and G. Li, *Chemical Reaction Polymerization* (ACS Symp. 364), 1988, p. 46.
- [5] J. Cabasso, *J. Appl. Polym. Sci.*, **13**, 1696 (1974).
- [6] J. L. Hendrick, H. R. Brown, and D. C. Hofer, *Polym. Prepr.*, **28**, 150 (1987).
- [7] A. J. Chalk and A. S. Hay, *J. Polym. Sci., Part A-1*, **7**, 691 (1969).
- [8] J. Liška and E. Borsig, *Chem. Listy*, **86**, 900 (1992).
- [9] J. Noda and J. Kagawa, *Kogyo Kagaku Zasshi*, **66**, 857 (1963).
- [10] H. Kawabe and M. Yanagita, *Bull. Chem. Soc. Jpn.*, **41**, 1518 (1968).
- [11] S. Dragan, J. Petrariu, and M. Dima, *J. Polym. Sci., Polym. Chem. Ed.*, **10**, 3077 (1972).
- [12] J. Liška, E. Borsig, and J. Tkáč, *Angew. Makromol. Chem.*, **211**, 121 (1993).

Received November 15, 1993

Revision received February 18, 1994