

**SOLID PHASE COSOLVENTS: POLYMER ANALOGS OF
N,N-DIALKYLAMIDES BASED ON POLYSTYRENE**

Václav JANOUT, Hana HRUDKOVÁ, Bohumír VALTER and Pavel ČEFELÍN

*Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, 162 06 Prague 6*

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Dedicated to Prof. O. Wichterle on the occasion of his 75th birthday.

Polymers of styrene of various type can be readily amidomethylated by a reaction with N-(hydroxymethyl)amides. Analogs of N-methyl-2-pyrrolidone, N-methyl-6-hexanelactam, N-methyl-8-octanelactam, and N,N-dimethylacetamide were prepared by the polymeranalogous amidomethylation. The reaction between poly(styrene-*co*-divinylbenzene) and N-(hydroxymethyl)-2-pyrrolidone proceeds by an acceleration mechanism. The extent of the reaction depends on the structure of the polymer and N-(hydroxymethylamide), on the concentration of the catalyst (trifluoroacetic acid) and on the way in which the polymer swells before the reaction. Polymers with bound residues of N-methylamide as solid cosolvents are catalysts of the model nucleophilic substitution reaction between sodium phenoxide and 1-bromooctane. A distinct polymer effect was recorded with polymer analogs of N-methyl-2-pyrrolidone in this reaction.

For many years now, polymers with bound functional groups imitating polar aprotic solvents have attracted attention because of their ability to activate anions in nucleophilic substitution reactions and to act as effective catalysts of reactions occurring by the transfer of the reactant through the phase boundary. In this way the catalytic effects of the polymer analogs hexamethylphosphorus triamide¹, N,N-dimethylacetamide^{1,2}, dimethyl sulfoxide^{3,4}, N-methyl-2-pyrrolidone^{5,6}, N,N-dimethylformamide⁷, and dimethyl sulfone⁸ have been documented.

Recently, we have published a preliminary report of an easy one-step procedure of preparation of the polymer analog of N-methyl-2-pyrrolidone based on cross-linked polystyrene consisting in the amidomethylation of poly(styrene-*co*-divinylbenzene) with the N-hydroxymethyl derivative of 2-pyrrolidone; the product was found to be an extremely effective catalyst⁶ under the conditions of a two-phase S-L and a three-phase L-S-L catalysis. The new study is concerned with the preparation of polymers based on various types of polystyrene with bound groupings imitating the structure of N,N-dimethylacetamide, N-methyl-2-pyrrolidone, N-methyl-6-hexanelactam, and N-methyl-8-octanelactam by the acid catalyzed amidomethylation of polymers with the corresponding N-(hydroxymethyl)amides and reported the

results of testing the effectiveness of such functionalized polymers as catalysts of nucleophilic substitution reactions.

EXPERIMENTAL

The infrared and ^1H NMR spectra were recorded, respectively, with a Perkin-Elmer 580 B and a Jeol PS 100 apparatus. The GLC analyses were carried out with a Chrom 5 apparatus (column 0.5×250 cm, SP 2 100 (5%), on Inerton AW-DMCS, N_2 as the carrier gas, FID).

Materials

Linear polystyrene, M_w 100 000, and poly(styrene-co-divinylbenzene), grain size 200–400 μm , were commercial products (United Chemical and Metallurgical Works, Ústí nad Labem, Czechoslovakia); the copolymer was extracted with tetrahydrofuran before use and dried at room temperature 48 h at 133 Pa. Polystyrene-*block*-poly(hydrogenated butadiene)-*block*-polystyrene, commercial Kraton G 1650 (Shell), M_w 74 000, PS content 28 wt. %, molar content of ethene/1-butene units 0.55, crosslinked by irradiation with accelerated electrons⁹.

N-(Hydroxymethyl)amides were prepared from the corresponding amides by a reaction with paraformaldehyde by employing a procedure analogous to the one reported earlier⁶: N-(hydroxymethyl)-2-pyrrolidone, m.p. 82–83°C; N-(hydroxymethyl)-6-hexanelactam, m.p. 63–65°C; N-(hydroxymethyl)-8-octanelactam, m.p. 53–57°C; N-hydroxymethyl-N-methylacetamide was used directly as a dry residue after the solvent had been distilled off on a rotational evaporator. All N-(hydroxymethylamides) had the corresponding ^1H NMR spectra.

Sodium phenoxide was prepared by reacting phenol with an equimolar amount of sodium methoxide in ethanol; the raw product was recrystallized from a hexane-benzene mixture (5 : 1 by vol.). All solvents were repurified before use by the usual methods, acetanhydride was repurified by distillation. Trifluoroacetic acid (Aldrich) and 1-bromooctane (Jansen) were used without further purification.

Amidomethylation of the Polymer

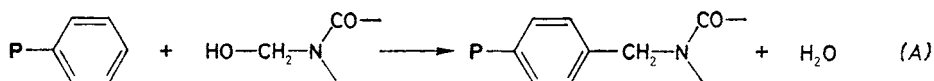
The starting polymer (0.10–0.75 g) was left to swell one hour in a chosen volume of chloroform in a closed flask. After that, N-(hydroxymethyl)amide and a mixture of trifluoroacetic acid and acetanhydride were gradually added, and the reaction mixture was maintained at 60°C for a chosen time with mild stirring. The soluble polymer was isolated by pouring out the reaction mixture into hexane (20 ml) and extracted with chloroform after separation, the insoluble (cross-linked) polymer was simply separated and washed successively with chloroform, tetrahydrofuran and ethanol prior to extraction. The polymers were dried at 35°C/133 Pa for 24 h.

The Reaction between Sodium Phenoxide and 1-Bromooctane

The polymer (0.020–0.074 g) was equilibrated with 0.5 ml of a 2M-solution of 1-bromooctane in anhydrous 1,4-dioxane at 75°C for 30 min. After that, 0.5 ml of a 0.5M-PhONa (solution in anhydrous 1,4-dioxane) was added, and the reaction mixture was vigorously stirred with a magnetic stirrer at 75°C (600 rpm). The concentration of the product (phenyl octyl ether) was followed by GLC (accuracy of determination 5%).

Amidomethylation of Polymers

Amidomethylation of aromatic compounds in order to introduce the amide or amino group is widely applied in organic chemistry¹⁰; in many procedures, N-(hydroxymethyl)imides are used in the reactions, due to the easier hydrolysis or hydrazinolysis of products. No systematic investigation of similar reactions of polymers used for their functionalization has yet been reported. Reactions of linear polystyrene (PS), crosslinked polystyrene (PS-DVB, with divinylbenzene in an amount 1–12 mole % as the crosslinking agent), or polystyrene-*block*-poly(hydrogenated butadiene)-*block*-polystyrene (PS-HB-PS) with N-(hydroxymethyl)amides were studied using findings obtained by the application of trifluoroacetic acid in generating the carbonium ion from the corresponding N-(hydroxymethyl)amides in a homogeneous medium and in the absence of the excess of water¹¹. Under these conditions, a reaction with aromatic compounds which are substituted is preferred:



Amidomethylations (A) were carried out at 60°C in chloroform in the presence of trifluoroacetic acid and of an at least equimolar amount of acetanhydride (related to amide) for binding water formed in the reaction. The course of the reactions was followed using the elemental analysis of isolated polymers. The structure was checked by IR spectra.

A very important factor affecting the degree of functionalization of the polymeric carrier, D_f , is the swelling of the starting polymer before the reaction (Table I). While the unswollen PS-DVB (2 mole %) does not react with N-(hydroxymethyl)-2-pyrrolidone, swelling of the polymer with already a small quantity of inert solvent prior to the reaction has a strong effect. If chloroform is added to the polymer simultaneously with the other reaction components in which the polymer does not swell, the reaction does proceed, but very reluctantly. A higher concentration of trifluoroacetic acid in the reaction mixture favourably affects the extent of the reaction, while the excess of the amidomethylation agent with respect to the polymer plays only an insignificant role.

Kinetic curves of the amidomethylation of poly(styrene-*co*-divinylbenzene) with N-(hydroxymethyl)-2-pyrrolidone (Fig. 1) show that the acceleration mechanism is strongly operative in the reaction of the polymer containing 1–4 mole % of the crosslinking agent, and that after a sufficiently long reaction time a high degree of functionalization can be reached, slightly depending on the content of the crosslinking agent. Acceleration may be due to the fact that during the reaction the originally hydrophobic polymer becomes a hydrophilic one, which swells increasingly more in the reaction medium. This is also suggested by the slow amidomethylation

of the less swelling PS-DVB (12 mole %), where only a very low functionalization is reached under the same conditions.

Under identical experimental conditions, polymers were amidomethylated with N-(hydroxymethyl)-2-pyrrolidone, N-(hydroxymethyl)-6-hexanelactam, N-(hydroxy-

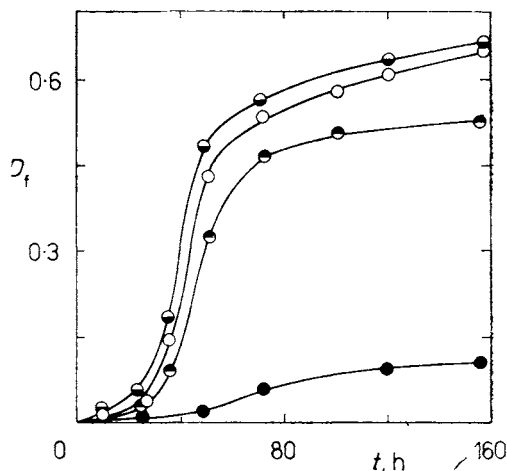
TABLE I

Dependence of the degree of functionalization, D_f , of the polymer PS-DVB (2 mole %) in a reaction with N-(hydroxymethyl)-2-pyrrolidone on the ratio of components of the reaction mixture (60°C, 72 h). The starting polymer was swollen in the given amount of CHCl_3 (1 h) before addition of the other components

Polymer mmol	CHCl_3 ml	Lactam mmol	$(\text{CH}_3\text{CO})_2\text{O}$ mmol	CF_3COOH ml	D_f
1.0	0	3.50	3.50	4	0.01
1.0	0.4	3.50	3.50	1.50	0.32 ^a
1.0	0.4	3.50	3.50	4	0.56
1.2	2	4.32	4.32	4	0.59
2.4	2	4.32	4.32	4	0.54
4.8	2	3.50	3.50	4	0.49

^a Without preswelling in CHCl_3 $D_f = 0.06$.

FIG. 1
The course of functionalization (of the degree of functionalization, D_f) of poly(styrene-co-divinylbenzene) in the reaction with N-(hydroxymethyl)-2-pyrrolidone (60°C). Content of the crosslinking agent (DVB, mole %): ● 1, ○ 2, ◐ 4, ● 12. Reaction mixture: 0.750 g (7.2 mmol) of polymer, 1.500 g (13 mmol) of lactam, 4.5 ml CHCl_3 , 3 ml acethanhydride, 12 ml trifluoroacetic acid



methyl)-8-octanelactam, and N-hydroxymethyl-N-methylacetamide; the effect of the type of the starting polystyrene carrier on the extent of the reaction was investigated using cases of the preparation of a polymer analog of N-methyl-2-pyrrolidone (Table II). Similarly to crosslinked polymers, the amidomethylation of polystyrene proceeds in a heterogeneous system, but the degree of functionalization reached is higher compared with D_f of slightly crosslinked polymers. Again, a distinctly lower D_f corresponds to the radically lower swelling of the strongly crosslinked polymer (12 mole % of the crosslinking component), and thus to the poorer accessibility of the polymer surface. The micellar type of the polymeric matrix with mobile short polystyrene chains arranged in the outer sphere of the crosslinked aliphatic nucleus PS-HB-PS represents a structure which, compared with the PS or PS-DVB structure, makes possible functionalization to distinctly higher degrees. Relations observed in the amidomethylation reactions with the other N-(hydroxymethyl)amides used are similar.

TABLE II

Polymer analogs of N,N-dialkylamides prepared by amidomethylation (60°C, 100 h). Reaction mixture: 2.4 mmol of the starting polymeric carrier, 8.6 mmol of N-(hydroxymethyl)amide, 2 ml CHCl_3 , 1 ml (10.6 mmol) of acetanhydride, 4 ml trifluoroacetic acid. D_f denotes the degree of functionalization

Polymer	Polymeric carrier	Functional group	Content of N mmol g^{-1}	D_f
I	PS	$\text{CH}_2\text{NCO}(\text{CH}_2)_2\text{CH}_2$	3.52	0.56
II	PS-DVB (1 mole %)	$\text{CH}_2\text{NCO}(\text{CH}_2)_2\text{CH}_2$	2.56	0.36
III	PS-DVB (2 mole %)	$\text{CH}_2\text{NCO}(\text{CH}_2)_2\text{CH}_2$	2.69	0.38
IV	PS-DVB (4 mole %)	$\text{CH}_2\text{NCO}(\text{CH}_2)_2\text{CH}_2$	2.45	0.34
V	PS-DVB (12 mole %)	$\text{CH}_2\text{NCO}(\text{CH}_2)_2\text{CH}_2$	0.65	0.08
VI	PS-HB-PS	$\text{CH}_2\text{NCO}(\text{CH}_2)_2\text{CH}_2$	1.97	0.95
VII	PS-DVB (2 mole %)	$\text{CH}_2\text{NCO}(\text{CH}_2)_4\text{CH}_2$	2.91	0.48
VIII	PS-DVB (2 mole %)	$\text{CH}_2\text{NCO}(\text{CH}_2)_6\text{CH}_2$	1.93	0.28
IX	PS-DVB (2 mole %)	$\text{CH}_2\text{N}(\text{CH}_3)\text{COCH}_3$	2.42	0.34
X	PS-HB-PS	$\text{CH}_2\text{N}(\text{CH}_3)\text{COCH}_3$	1.36	0.63

Polymers I–X as Solid Cosolvents

Polymers I–X (Table II) are polymer analogs of the usual and untypical polar aprotic solvents. In order to investigate the effect of polymer structure on polymer activity in catalysis, we investigated the efficiency of these solid cosolvents in the activation of anions in a reaction between sodium phenoxide and an excess of 1-bromooctane in anhydrous 1,4-dioxane at 75°C. The reaction virtually does not proceed in the absence of the cosolvent (homogeneous reaction). In the presence of the functionalized polymer, the extent of the reaction is above 0.6 after 22 hours, with phenyl octyl ether as the only reaction product. The observed reaction constants, k_0 , correspond to the second-order kinetics and increase with the increasing concentration of functional groups of the polymer in the reaction mixture, c (Fig. 2). The dependence confirms that the polystyrene matrix does not contribute to the catalytic efficiency of the solid cosolvent (for $c \rightarrow 0$, k_0 equals k_0 in the homogeneous reaction)¹². Using k_0 values, the specific rate constants, $k_s = k_0/c$, were calculated (Table III). Under standard conditions, it may be assumed that the k_s values depend only on the chemical and physical nature of the polymer, and thus characterize the effect of functional groups on the given polymeric carrier (independently of D_f); if need be, they allow us to estimate the effect of the type of the polymeric matrix on

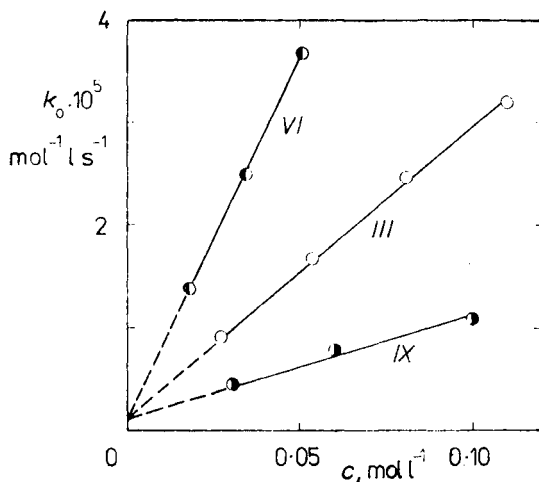


FIG. 2

Dependence of the observed rate constant, k_0 , of the reaction between sodium phenoxide (0.25 mmol) and 1-bromooctane (1.00 mmol) in anhydrous 1,4-dioxane (1 ml) at 75°C on the amount of the polymeric catalyst III, VI, or IX (c is the concentration of functional groups of the polymer in the reaction mixture)

the activity of the polymeric catalyst. On the other hand, however, in applications of the polymer of type *III* under comparable conditions, the k_s values increase with increasing degree of functionalization, i.e. with increasing nitrogen content in the polymer (Fig. 3). This phenomenon is related to the mutual cooperation of functional groups in their interaction with the ionic pairs of sodium phenoxide. A monotonic increase in k_s with increasing content of functional groups imitating a dipolar aprotic solvent need not be a general phenomenon: e.g., in the case of a polymer analog of dimethyl sulfoxide based on polystyrene, an activity maximum was observed, corresponding to the optimal content of hydrophilic (functionalized) units in the polymer¹³.

A comparison of the k_s values in reactions in the presence of N-methyl-2-pyrrolidone and in the presence of its polymer analogs *I–IV* reveals a weaker specific activity of free lactam, and thus the so-called polymer effect. At the same time, the dependence of k_s on the degree of crosslinking of the polymeric matrix at a 1–4 mole % content of the crosslinking agent (polymers *II–IV*) is not pronounced, while a further

TABLE III

Catalyzed reaction between sodium phenoxide (0.25 mmol) with 1-bromooctane (1.00 mmol) in anhydrous 1,4-dioxane (1 ml) at 75°C. DVB denotes the content of divinylbenzene units in the polymeric catalyst, c is the concentration of functional groups in the reaction mixture, k_s is the specific rate constant ($k_s = k_0/c$)

Catalyst	[DVB] mole %	N mmol g ⁻¹	c mol l ⁻¹	$k_s \cdot 10^5$ mol ⁻² l ² s ⁻¹
None	—	—	—	0.1 ^a
N-Methyl-2-pyrrolidone	—	10.1	0.10	16
Polymer <i>I</i>	0	3.52	0.09	26
Polymer <i>II</i>	1	2.56	0.10	20
Polymer <i>III</i>	2	2.69	0.11	29 (29) ^b
Polymer <i>IV</i>	4	2.45	0.10	19
Polymer <i>V</i>	12	0.65	0.10	10
Polymer <i>VI</i>	—	1.97	0.05	73 (75) ^b
Polymer <i>VII</i>	2	2.91	0.07	18
Polymer <i>VIII</i>	2	1.93	0.06	22
N,N-Dimethylacetamide	—	11.5	0.10	17
Polymer <i>IX</i>	2	2.42	0.06	13
Polymer <i>X</i>	—	1.41	0.10	18

^a k_0 is in mol⁻¹ l s⁻¹ (extent of reaction 0.09 after 22 h)¹²; ^b with the catalyst repeatedly used.

increase in the degree of crosslinking (polymer V) has an unfavourable effect. If, however, pyrrolidone units have been immobilized in the micellar type of the polymeric matrix, the polymer effect is particularly marked: in the case of application of polymer VI the k_s value is almost five times higher than in the case of N-methyl-2-pyrrolidone alone. This suggests an important role played by hydrophilic-hydrophobic relations (a similar phenomenon has also been observed with a polymer containing sulfoxide units based on poly(vinyl alcohol-co-ethylene))¹², or an easy accessibility of catalytic sites.

Polymers with bound units of a seven- and nine-membered lactam (polymers VII and VIII) possess a catalytic activity close to that of polymers containing pyrrolidone units. On the contrary, a polymer analog of N,N-dimethylacetamide based on PS-DVB (polymer IX) is little effective in the activation of the phenoxide ion, and no polymer effect has been recorded. Substitution of the porous carrier with a micellar carrier caused an increase in k_s (polymer X), but the increase was by no means as pronounced as in the case of the polymer containing pyrrolidone units. A similarly weak activity of other polymer analogs of N,N-dialkylacetamide has also been observed in other studies^{1,14}.

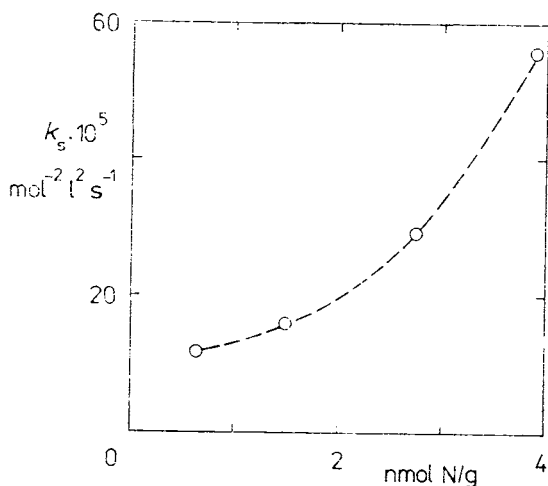


FIG. 3

Catalysis of the reaction (specific rate constant, k_s) between sodium phenoxide (0.25 mmol) and 1-bromooctane (1.00 mmol) with poly(styrene-co-divinylbenzene) 98:2 mole % containing N-methyl-2-pyrrolidone functional units (content in mmol N per one gram of the catalyst) at 75°C in anhydrous 1,4-dioxane. In place of nmol should be mmol (axis x)

The easy preparation of a polymer analog of N-methyl-2-pyrrolidone based on polystyrene and the high activity of this solid cosolvent in the catalysis of organic reactions suggests that it may be applied on a wide scale.

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