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SOLID-PHASE COSOLVENTS.
A POLYMER ANALOG OF N-METHYL-2-PYRROLIDONE BASED ON CROSSLINKED POLYSTYRENE

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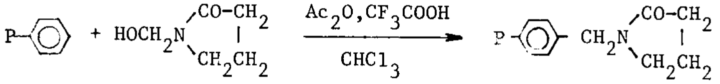
SUMMARY: Polymer analogs of N-methyl-2-pyrrolidone were prepared by reacting crosslinked polystyrene with N-hydroxymethyl-2-pyrrolidone. These polymers are effective catalysts of nucleophilic substitution reactions carried out under liquid-solid (L-S) and liquid-solid-liquid conditions.

N-Methyl-2-pyrrolidone (NMP) is known as a polar aprotic solvent which effectively accelerates nucleophilic substitution reactions[1]. Similarly to other solvents possessing similar properties (dimethylsulfoxide, N,N-dimethylformamide, N,N-diethylacetamide, hexamethylphosphortriamide), its application is restricted with respect to several facts: (i) Difficulties arising in the isolation of products from the reaction mixture. (ii) A property common to the group of polar aprotic solvents is their high solvation power and high miscibility both with organic solvents and with water. In handling with toxic compounds dissolved in such solvents, contact of the solution with skin may lead to the penetration of the toxic compounds into tissues and thus to intoxications[1]. (iii) A comparatively high price of NMP.

In connection with the development of the concept of three-phase catalysis[2], an investigation was begun of polymer analogs of these solvents with a view to their use as solid cosolvents and catalysts[2,3]. Up to now, polymers bearing bound groups and having a structure analogous to HMPT[4,5], DMSO[6-8], DMF[9], dialkylacetamide[10], dimethylsulfone[11] have been described, but only poly(n-vinyl-2-pyrrolidone)[12-14] has been studied with attention as a model for the investigation of the properties of a polymer analog of NMP. However, the results obtained in the catalysis of nucleophilic substitution reactions were not very encouraging. This may be due to the fact that poly(N-vinyl-2-pyrrolidone) is not a too suitable structural model for modelling properties similar to those of NMP: in this model, the structural unit which plays the key role in the catalysis is part of the main chain as a constitutional repeat unit. At the same time, it is known that it is just the increase in the mobility of catalytically active functional groups due to the increase in their distance from the main polymer chain (by means of a spacer) that considerably affects the rise in their catalytic activity[2,3].

In this study we report a new easy method of preparation of a polymer analog of NMP based on polystyrene crosslinked with divinylbenzene (DVB) and data which demonstrate its great ability to catalyze nucleophilic substitution reactions. Polymers (1)-(4) are formed by a reaction between crosslinked polystyrene (PS-1% to 4% DVB) and N-hydroxymethyl-2-pyrrolidone in the presence of acetanhydride and trifluoroacetic acid:



(1)-(4)

(1) 1% DVB, 35% r.s., 2.56 mmol N/g
(2) 2% DVB, 38% r.s., 2.69 mmol N/g
(3) 2% DVB, 18% r.s., 1.50 mmol N/g
(4) 4% DVB, 33% r.s., 2.45 mmol N/g

Thus, e.g., polymer (2) was prepared from 0.500 g poly[styrene(98)-co-divinylbenzene(2)] (microporous, gel type, grain size 160-400 µm) preswollen with 2.00 ml $CHCl_3$ (30 min., room temperature), to which 1.000 g N-hydroxymethyl-2-pyrrolidone (8.70 mmol)[15], 2.16 g acetanhydride (2.00 ml, 21.2 mmol) and 8.00 ml CF_3COOH were added. The reaction mixture was kept in a closed flask at 58°C for 115 h. After that, the polymer was filtered, washed with $CHCl_3$, extracted with THF (Soxhlet, 5 h), and dried (50°C, 24 h, 13.3 Pa). 0.615 g of polymer (2) was obtained. IR spectrum (KBr disc, cm^{-1}): 3080,3060,3020,2920,2850,1685,1610, 1580,1510,1500,1460,1450,1420,1390,1360,850,810. Polymers (1), (3), (4) were prepared in a similar manner[16].

The catalytic activity of polymers (1)-(4) was tested in reactions of 1-bromooctane with sodium phenoxide carried out under the L-S conditions (dioxan, 75°C) and with potassium thiocyanate carried out under the L-S-L conditions (toluene-H_2O, 100°C). In the former case the crosslinked polymer acts as a solid cosolvent, in the latter it plays the role of a mediator for the transfer of reactants through the phase boundary. The results are summarized in the Table.

In the two-phase L-S conditions the activating influence of polymers may be explained by an effect upon the cation-anion bond formed in interactions between the ionic pairs present in solution and functional groups of the polymer, and/or by effects of a local rise in the concentration of reaction components inside the polymer matrix. Only a simultaneous effect of these two factors may explain the finding that the specific rate constant, k_{sp}, which expresses the specific reaction rate at a unit concentration of functional groups of the polymers is even higher in the case of polymer (2), than in the case of a reaction in the presence of NMP alone. On the other hand, if crosslinked poly(N,N-dialkylacrylamide) is used as the polymer analog of N,N-diethylacetamide under completely analogous conditions, no such effect could be observed[10]. Of course, also in this polymer analog the structural model unit of N,N-dialkylacetamide is part of the main polymer chain. With the degree of functionalization of the polymer analog of NMP decreasing to approximately half its value (cf. polymers (2), (3)), the specific activity, i.e., k_{sp}, decreases accordingly. Even if the degree of crosslinking of these polymer catalysts is considerably increased, there is no pronounced drop in their activating influence. This suggests that interactions which are necessary for the activation of the phenoxide anion do not necessarily require a conforma-

Table. Nucleophilic substitution on 1-bromooctane catalyzed by polymer analogs of NMP (1)-(4)

Nucleophile	Catalyst mmol	k_{obs}[a]	ξ[b](%)	k_{sp}[c]
PhONa[d]	-	-	9	-
	PS-2%DVB	-	9	-
	NMP; 0.101	1.60	69	15.8
	(1); 0.100	2.05	76	20.5
	(2); 0.108	3.11(3.14)[e]	89(90)[e]	28.8(29.1)[e]
	(2); 0.054	1.54	66	28.5
	(3); 0.100	1.58	64	15.8
	(4); 0.100	1.90	74	19.0
KSCN[f]	-	-	0	-
	PS-2%DVB	-	0	-
	NMP; 0.200	-	2	-
	(1); 0.130	1.23(1.26)[e]	97(98)[e]	9.46(9.69)[e]
	(1); 0.065	0.89	92	13.7
	(2); 0.135	0.98	93	7.26
	(3); 0.075	0.27(0.25)[e]	55(53)[e]	3.60(3.33)[e]
	(4); 0.125	0.76	98	6.08

[a] k_{obs} - rate constants determined from eight measurements; for the reaction of PhONa second-order kinetics (1x mol^{-1}s^{-1}, for the reaction of KSCN pseudomonomolecular second-order kinetics (min^{-1}). [b] Extent of the reaction in the case of sodium phenoxide, 22 h, in the case of reactions of KSCN calculated as the average from the determination of the concentrations of 1-bromooctane and octylthiocyanate, 48 h. Analysis of the reaction mixtures: GLC using Chrom 51, steel column 0.3 x 150 cm, 10% OV 17 using chromaton N-AW HMDS, carrier gas N_2, FID. Accuracy of the concentration determination was 3%. [c] $k_{sp} = k_{obs}/c_{cat}$, where c_{cat} is the "concentration" of functional groups of the catalyst in the organic phase; unit for the reaction of PhONa in 1^{2}mol^{-2}s^{-1}, for the reaction of KSCN in 1 mol^{-1}min^{-1}. [d] To 20-67 mg of polymer (or to 25 mg PS-2%DVB) equilibrated 2 h with 0.5 ml of 0.5 M $C_8H_{17}Br$ in anhydrous 1.4-dioxan (dodecane as the internal standard) at 75°C, 0.5 ml of 2M sodium phenoxide in 1.4-dioxan was added. The mixture was stirred with a magnetic teflon stirrer and kept in a closed test tube at 75°C for 22 h. [e] In the re-use. The polymer was separated after the given time, washed with the respective solvent (1.4-dioxan or toluene) and used by employing the same procedure as in the first experiment. [f] To 25-50 mg of polymer (1)-(4) (or 50 mg of PS-2%DVB) equilibrated with 1 ml of 0.6M 1-bromooctane in toluene at 100°C, after one hour 2 ml of aqueous 13M KSCN was added and the mixture was stirred with a magnetic teflon stirrer in a closed test tube at 100°C for 48 h.

tional reorganization of the polymer matrix (cf. polymers (1), (4)). The same polymers (1), (4) possess a high catalytic activity also under the three-phase L-S-L conditions. Under similar conditions, the polymer analog of N,N-dialkylacetamide is either completely inactive, or its catalytic activity is very low[10]. The results obtained with poly(N-vinyl-2-pyrrolidone) under three-phase conditions are not satisfying either[14]. Thus, while in the reaction of 1-bromooctane with alkali iodides in the presence of the catalytically most active crosslinked poly(N,N-dioctylacrylamide) the conversion reached in the toluene/H_2O system at 90°C after 24 h is 36%, and that reached in the presence of the crosslinked poly(N-vinyl-2-pyrrolidone) is 66%, in the case of polymer (3) and under analogous conditions a 98% conversion is reached after 10 h.

Compared with the other polymers modelling the structure of amide solvents and described so far, the polymer analog of NMP has the following advantages: (i) it is readily available by means of a functionalization reaction of the structurally well defined polymer carrier, (ii) it possesses a high catalytic activity. Further aspects of the application of these polymers in catalysis are being investigated and will be reported.

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15. N-Hydroxymethylpyrrolidone was prepared by a reaction of 2-pyrrolidone (17.000 g, 200 mmol) with paraformaldehyde (6.000 g, 200 mmol) in ethanol (100 ml) in the presence of 0.100 g anhydrous Na_2CO_3 (0.1 g, 1.0 mmol) at 50°C. The raw product was recrystallized from the mixture EtOH-Et_2O (2:1), yield 16.310 g (71%), m.p. 82-3°C.
16. Elemental analysis (Calculated/found,%): (1) C = 84.81/84.72; H = 7.58/7.46; N = -/3.58. (2) C = 84.34/84.08; H = 7.57/7.39; N = -/3.77. (3) C = 87.93/87.49; H = 7.62/7.50; N = -/2.10. (4) C = 95.14/84.91; H = 7.58/7.49; N = -/3.43.

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