Polymer Bulletin 15, 485–490 (1986)

Polymer Bulletin

Polymer-Supported Oligo(N-Acetyliminoethylenes)

New Phase Transfer Catalysts

J. Kahovec*, M. Jelínková, and V. Janout

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences,
CS-162 06 Prague 6, Czechoslovakia

Summary

Oligo(N-acetyliminoethylenes), both free and grafted on polystyrene, polymethacrylate and cellulose were prepared by the ring-opening polymerization of 2-methyloxazoline. Their phase transfer catalytic activity in nucleophilic substitution reactions was examined.

Introduction

Polymers functionalized with groups having the dipolar aprotic solvent structure are active as catalysts in nucleophilic substitution reactions. Such polymers called solid solvents or solid cosolvents accelerate reactions of anions with organic substances performed in a two-phase or three-phase arrangement. Active functional groups are, e.g., hexamethylphosphortriamide (1,2), dimethyl sulfoxide (3) or glyme analogs (4). N,N-dialkylcarboxamides rank among the most important dipolar aprotic solvents. Of their polymer analogs, only poly(N,N-dialkylacrylamides) (5), poly(N-vinylpyrrolidone) (6,7) and poly[N-methyl-N-(p-vinylbenzyl)formamide] (8) have been studied.

In this communication, oligo(N-acetyliminoethylenes) with the structure $(N(COCH_3)CH_2CH_2)_n$ or those immobilized on a proper polymer carrier are described. The preparation of these polymeric models of N,N-dimethyl- or N,N-diethylacetamide, as well as their use as catalysts in some nucleophilic substitution reactions, both in a two-phase and three-phase arrangement, is reported.

At the same time, the effect of the polymer carrier and the effect of the multiplicity of active groups (n) on their catalytic activity are examined.

Experimental

Materials

1a chloromethylated styrene - divinylbenzene copolymer, Cl content 19.82%, surface area 0.01 m^2/g; 1b chloromethylated macroporous styrene - divinylbenzene copolymer, Cl content 17.45%, surface area 10.3 m^2/g; 1c tosylated macroporous 2-hydroxyethyl methacrylate (76%) - ethylene dimethacrylate (24%)

---

* To whom offprint requests should be sent

copolymer was prepared by a reaction of the copolymer with an equimolar amount of p-toluenesulfochloride in dry pyridine, S content 4.72%, N content 0.82%, surface area 21.7 m^2/g; 1d macroporous copolymer 2-(4-toluenesulfonyloxy)ethyl methacrylate - ethylenedimethacrylate, S content 5.42%; surface area 52.5 m^2/g; 1e macroporous copolymer 2.3-epoxypropyl methacrylate (60%) - ethylene dimethacrylate (40%), surface area 54.3 m^2/g; 1f tosylated cellulose prepared by a reaction of bead cellulose with an excess of p-toluenesulfochloride in dry pyridine, S content 6.35%; N,N-diethylacetamide, prepared from diethylamine and acetic anhydride, b.p. 181°C, assay (GLC) 96.2%; 2-methyloxazoline, prepared according to the literature (9), dried with molecular sieves, assay (GLC) 99.1%.

Preparation of polymeric catalysts

A mixture of the alkylating polymer 1a-1f and 2-methyloxazoline (in molar ratios 1:20 to 1:30 for 1a, 1b, 1e, 1:50 to 1:80 for 1c, 1d, 1f) was heated while shaking in a sealed ampoule to 80°C for 24 h. Homopolymer (3) of 2-methyloxazoline was dissolved in methanol, and the graft copolymer (2) was extracted with methanol in Soxhlet apparatus for 12 h. Homopolymers (3) were obtained by evaporating methanolic solutions. All polymers were dried in vacuo at 50°C. Properties of the products are given in Table 1.

Table 1. Properties of polymeric catalysts[a]

No.	N %	$NAcCH_2CH_2$ mmol/g	n[b]	No.	N %	$NAcCH_2CH_2$ mmol/g	n[b]
2a	11.95[c]	8.53	5.6	2f	9.11[e]	6.50	7.4
2b	6.58[d]	4.70	1.6				
2c	7.56	5.40	6.8	3c	15.38[f,i]	10.99	-
2d	7.46	5.32	5.8	3d	15.61[g,i]	11.15	-
2e	2.05	1.46	-	3f	14.87[h,i]	10.62	-

[a] All 2 and 3 strongly absorb in the IR region at 1635-1640 cm^{-1}. [b] Average degree of polymerization of grafts (n) was calculated from N and Cl (or S) contents of polymers 2 and 4, respectively. [c] Cl content 1.85%. [d] Cl content 7.43%. [e] S content 2.42%. [f] M.p. 70-93°C. [g] M.p. 110-125°C. [h] M.p. 50-65°C. [i] NMR data ($CDCl_3$) for 3 : 7.93(s), CH_3CO; 6.61(s), CH_2; intensity ratio 3:4.

Catalyzed reaction of 1-bromooctane with nucleophiles

A mixture of the polymer catalyst and a solution of 1-bromooctane in 1,4-dioxane or toluene was stirred magnetically (Teflon rod 10 mm) at the reaction temperature for 30 min. After adding a solution of nucleophile in dioxane or toluene and dodecane as an internal standard, the reaction mixture was intensively stirred (600 rpm) at the reaction temperature and

Table 2. Oligo(N-acetyliminoethylenes) as catalysts in reactions of octyl bromide with nucleophiles

Catalyst	KSCN[a]		NaI[a]		PhONa[b]	
	yield[c] %	rel.[e] activity	yield[c] %	rel.[e] activity	yield[d] %	rel.[e] activity
2a	14	1.0	8	1.0	19	1.0
2b	7	0.9	4	0.9	24	2.3
2c	22	2.5	11	2.2	72	6.0
2d	16	1.8	2	0.4	61	5.1
2e	18	7.3	10	7.1	25	7.4
2f	10	0.9	1	0.2	17	1.2
3c	35	1.9	14	1.4	46	1.9
3d	2	0.1	2	0.2	20	0.8
3f	26	1.5	9	0.9	40	1.7
AcNEt$_2$	48	3.4	4	0.5	85	4.4
PS-DVB[f]	< 1	-	0	-	10	-
HEMA[g]	3	-	2	-	20	-
Ⓒ[h]	6	-	0	-	11	-
none	0	-	< 1	-	9	-

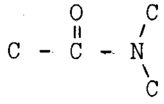
[a] 0.5 ml 0.6M octyl bromide in toluene, 50 mg catalyst, 1.0 ml aq. 6M KSCN or 6M NaI, 100°C. [b] 0.5 ml 2M octyl bromide in 1,4-dioxane, 25 mg catalyst, 0.5 ml 0.5M sodium phenoxide in 1,4-dioxane, 75°C. [c] After 48 h. [d] After 22 h. [e] See Experimental. [f] Styrene-2% divinylbenzene copolymer. [g] Separon H 100 (see 1c in Materials). [h] Bead cellulose.

analyzed by GLC. The reaction yields were calculated from concentration of octyl derivatives and from the 1-bromooctane decrease. The specific yields were obtained by calculating the yields per 1 mmol of N(COCH$_3$)CH$_2$CH$_2$ grouping present in the catalyst. The relative activities of catalysts were obtained by dividing the individual specific yields by the specific yield of reaction performed in the presence of the polystyrene-based catalyst 2a (its relative activity is arbitrarily put to unity).

Results and Discussion

One of the ways for improving the activity of catalyst is enhancement of the local concentration of catalytically active groups. This can mostly be achieved by building them on or into a polymer chain. Another possibility of modifying the activity of a catalyst is a change in the polarity or hydrophilicity (hydrophobicity) of the microenvironment of catalytically active groups. In the case of immobilized polymer-supported catalyst this can be achieved by an appropriate choice of the polymer carrier.

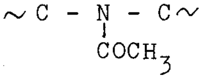
The N,N-dialkylcarboxamide grouping 4 present in the best dipolar aprotic solvents (N,N-dimethylformamide, N,N-dimethylacetamide, N,N-diethylacetamide, N-methylpyrrolidone) can be arranged into a polymer chain by connecting either acyl or amine carbon atoms. Poly(N,N-dialkylacrylamides) 5 derived from the grouping 4 by connecting acyl moieties to the aliphatic main chain proved to be solid phase cosolvents (5). By connecting amine alkyls, a polymer chain of the type 6 is formed. As far as we know, the catalytic activity of this type of substances has not yet been examined.



4

$\sim CH_2\underset{CONR_2}{CH}\sim$

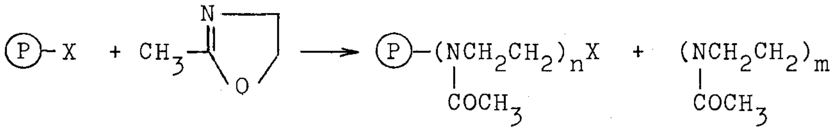
5



$\sim C - \underset{COCH_3}{N} - C\sim$

6

The catalysts-oligo(N-acetyliminoethylenes), free (3) or grafted on various polymer carriers (2), were prepared by the reaction of polymeric alkylating derivatives 1 with 2-methyloxazoline (Eq.1)



(1)

1 2 3

where Ⓟ denotes the polymer skeleton (crosslinked polystyrene, crosslinked polymethacrylate, cellulose) and X is the alkylating group (chlorine, tosylate, epoxide). This grafting reaction has been described in the literature for crosslinked polystyrene (10) and PVC (11). Grafted copolymers 2c-2f in Table 2 have not been described up to the present time. The average degree of polymerization in grafts was calculated from the nitrogen content in products 2 and from the chlorine or sulfur content in the starting polymer 1, assuming that all alkylating groups present initiate the polymerization of 2-methyloxazoline. The graft length (n in Table 1) in polymer-supported catalysts is rather small (cf. ref. 10), obviously due to an insufficient excess of 2-methyloxazoline relatively to the initiating alkylating groups of the polymer carrier and to contaminants present in the starting 1. In all grafting reactions, homopolymer (3) of 2-methyloxazoline is formed. In the preparation of 2c, 2d, 2f the conversion of 2-methyloxazoline to the homopolymer goes up to 20 - 30%, obviously because of the initiation with traces of acid formed in the synthesis of the corresponding alkylating polymers.

The synthesized free 3 and polymer-supported oligo(N-acetyliminoethylenes) 2 were tested as catalysts in the reactions (2)-(4)

$$C_8H_{17}Br + KSCN \longrightarrow C_8H_{17}SCN + KBr \quad (toluene\text{-}H_2O) \qquad (2)$$

$C_8H_{17}Br + NaI \longrightarrow C_8H_{17}I + NaBr$ (toluene-H_2O) (3)

$C_8H_{17}Br + C_6H_5ONa \longrightarrow C_8H_{17}OC_6H_5 + NaBr$ (dioxane) (4)

The activity of the catalysts was evaluated by determining yields of the reactions performed under standard conditions. Residual alkylating groups in the catalysts may compete with octyl bromide in its reactions with nucleophiles, and thus affect the yields. This distortion is apparently not essential, due to small amounts of the catalysts used and due to the assumed inaccessibility of the residual alkylating groups. Evaluation of relative activity of the catalysts in the reactions is rather a difficult task, due to different polymer carriers and to the broad range of loading of the active groups. In the end, the relative activities were calculated from the specific yields (see Experimental). The relative activities thus obtained are doubtless a rough measure: they suffer from unprecise analyses, different accessibility, mutual influence of the active groups, and other factors. In spite of this, it is possible, basing on the relative activities of the catalysts, to draw some qualitative conclusions:

- Of the polymer-supported catalysts, the ones with the polymethacrylate skeleton are generally the most active. At the same time, under the conditions of three-phase catalysis (Eq. 2 and 3) the most active catalysts are those with a low loading of N-acetyliminoethylene groups, in two-phase reactions (Eq. 3) those with both low and high loading.
- Non-supported oligo(N-acetyliminoethylenes) are generally little active. In spite of that, due to a considerable cumulation of the active groups, they can give fair yields of products. Their drawback is a considerable solubility in water or dioxane, consequently, their recoverability is practically impossible.
- Polystyrene-supported catalysts, both micro- and macroporous, are in all reactions relatively little active.
- Cellulose-supported catalyst is little active in all reactions (in accord with ref. 12).

The catalytic activity of a polymer-supported phase transfer catalyst is affected by many factors, such as chemical structure of the carrier, its hydrophilic or hydrophobic properties, porosity, degree of crosslinking, concentration and distribution of active groups. Hence, it is very difficult to draw general conclusions about the effect of a single factor. Nevertheless, it seems (cf. catalysts 2c and 2e) that cumulation of $N(COCH_3)CH_2CH_2$ active groups in polymer-supported catalysts does not bring about any significant enhancement of their activities, at least in the three-phase arrangement (cf. an analogous adverse effect of cumulation of sulfoxide groups in DMSO-immobilized catalysts (13)).

The results roughly confirm the findings of other authors (8,14) and ours (3) about the adverse effect of the absence of hydrophobic domains in a catalyst on its solid solvent activity in nucleophilic substitution reactions (see 2f, 3c, 3d, 3f).

References

1. S.L.Regen, A.Nigam, J.J.Besse, Tetrahedron Lett. 1978, 2757
2. M.Tomoi, M.Ikeda, H.Kakiuchi, Tetrahedron Lett. 1978,3757
3. V.Janout, J.Kahovec, M.Hrudková, F.Švec, P.Čefelín, Polymer Bull. 11, 215 (1984)
4. J.G.Heffernan, W.M.MacKenzie, D.C.Sherrington, J.Chem. Soc., Perkin Trans. II 1981, 514
5. S.L.Regen, A.Mehrotra, A.Singh, J.Org.Chem. 46, 2182 (1981)
6. N.Yamazaki, A.Hirao, S.Nakahama, Polymer J. 7, 402 (1975)
7. M.Jelínková, J.Kahovec, F.Švec, Polymer Preprints 26 (1), 84 (1985)
8. S.Kondo, Y.Inagaki, K.Tsuda, J.Polymer Sci., Polymer Lett. Ed. 22, 249 (1984)
9. H.Witte, W.Seeliger, Liebigs Ann.Chem. 1974, 996
10. T.Saegusa, S.Kobayashi, A.Yamada, Macromolecules 8, 390 (1975)
11. P.D.Trivedi, D.N.Schulz, Polymer Bull. 3, 37 (1980)
12. A.Akelah, D.C.Sherrington, Eur.Polymer J., 18, 301 (1982)
13. V. Janout, H.Hrudková, P.Čefelín, Collect.Czech.Chem. Commun. 49, 2096 (1984)
14. S.Kondo, K.Ohta, R.Ojika, H.Yasui, K.Tsuda, Makromol.Chem. 186, 1 (1985)

Accepted June 7, 1986

C