NOTES

New Carboxylated Mo(VI)-Grafted Poly(amidoamine) Resins as Heterogeneous Oxygen Transfer Catalysts

It is well-known that compounds of Mo(VI) with carboxylic acids are powerful catalysts for the epoxidation of olefins.[1,2] To this purpose, a commercial carboxylated resin has been used by Ivanov and co-workers,[3] in order to heterogenize the Mo(VI) derivatives. A weak point of using commercial resins is that is not possible to control the number and distribution of the carboxylic groups. This results in poor flexibility of structure and properties of the final catalyst: in other words, it is not possible to "tailor-make" the catalyst. We thought it interesting to report here our preliminary results concerning the synthesis, Mo(VI) grafting, and catalytic activity of a multifunctional carboxylated resin. This product constitutes the first example of a new family of tailor-made oxygen transfer catalysts. The resins have a mixed poly(amidoamine)–poly(vinylpyrrolidone) structure. It is known that polyamidoamines, either linear or crosslinked, provide a very convenient way to obtain macromolecular multifunctional structures.[4,5] Some crosslinked polyamidoamines have been already studied as selective ion exchange resins.[6,7]

EXPERIMENTAL

Materials

1,4-Bisacryloylpiperazine (BP) was prepared as previously described.[8] *N,N'*-Ethylenediaminodiacetic acid (EDDA) (99% pure) was purchased from Fluka and used without further purification. Triethylamine (TEA) (Aldrich, 99% pure) was used as received. *N*-Vinylpyrrolidone (VIP) (Aldrich) was distilled under reduced pressure just before use. 2,2-Azo-bis(2-methylpropionitrile) (AIBN) (Fluka 99%) was recrystallized just before use by dissolving, at room temperature, in chloroform (10 mL/g), filtering, and diluting with *n*-heptane or ether (20 mL/g).

Instruments and Methods

The surface areas defined according to the well-known Brunauer, Emmet, and Teller method (BET areas) were calculated by using a Carlo Erba Sorptomatic apparatus. The Mo/CO_2H ratio in the grafted catalysts was evaluated by determining CO_2H groups acidimetrically, and molybdenum by atomic absorption (Varian AA-475) after solubilization of the grafted sample by a preliminary chemical attack. Infrared spectra (KBr) were recorded on a Perkin-Elmer 782 spectrophotometer. The catalytic activity of the grafted catalysts was determined either by epoxidizing cyclohexene with hydroperoxides[9] or by performing the Baeyer-Villiger oxidation of cyclopentanone to δ-valerolactone. The appearance of epoxide was followed by direct titration of oxirane oxygen,[10] coupled with simultaneous gas chromatographic analyses (with Carlo Erba Instrument), and the disappearance of hydroperoxide by iodometric titration. The appearance of δ-valerolactone was followed as reported in literature.[11]

PREPARATION OF THE RESINS

The synthesis of the most catalytically active resin (EGDA) is given. BP (3.8848 g, 0.020 mol) and EDDA (2.4668 g, 0.014 mol) were dissolved in water (20 mL). To this solution, TEA (1.45 g, 2.0 mL) was added, the mixture was stirred by hand until homogenous, and left to stand in the dark at room temperature for 24 h. VIP (8 g, 0.075 mol) and finely powdered AIBN (0.081 g, 0.5 mmol) were then added; the reaction vessel was carefully purged with nitrogen and maintained at 50 ± 1°C for an additional 24 h with occasional stirring. The resulting solid gel was recovered, ground, and carefully washed with water until no extractables were present in the liquors after 24 h standing. The product was finally dried to constant weight at room temperature and 0.07 torr.

Yield was 11.53 g. The resin had 2.5 meq CO_2H/g. Other similar resins can be prepared exactly in the same way by substituting equimolecular amounts of ω-amino acids (for instance, glycine, β-alanine, ϵ-aminocaproic acid, etc.), for EDDA, and enough TEA to neutralize the carboxylic groups present.

PREPARATION OF THE Mo(VI)-GRAFTED RESINS EGDA–Mo(VI)

Relative to the grafting procedure reported by Ivanov et al.[3] that implies HCl removal by chemical interaction between an alcoholic solution of $(MoO_2)_n Cl_m$ and the carboxylic functional groups of the resin, we have found that our procedure[12] is more reliable.

According to this procedure the Mo(VI) fixation is carried out under acids conditions (1.0 $< pH < 3.0$) by water elimination between molybdic acid and the surface carboxylic acid groups. The grafting procedure is conveniently carried out in dioxane/water (40/30, v/v), while the removal of water is performed by azeotropic distillation under mild experimental conditions. As usual, the grafted catalysts are thoroughly washed (water, dioxane, and diethylether) before drying under vacuum, and using.

The Mo content of the resin was obtained by atomic absorption after a preliminary chemical attack and solubilization of the grafted sample. The presence of the MoO_2 group in the grafted resin has been confirmed by IR spectroscopy. The typical symmetric and asymmetric stretching vibrations of this moiety are found at 970 and 905 cm^{-1}, respectively. After Mo(VI) fixation the BET area of the resin greatly increases (159.288 m^2/g).

RESULTS AND DISCUSSION

Synthesis

The synthesis of the resin considered in this study was performed in two steps. First, a poly(amidoamine) prepolymer was prepared by Michael-type polyaddition of either N,N'-ethyl-enediaminodiacetic acid (EDDA), or other ω amino acids, to 1,4-bisacryloylpiperazine, in a way similar to that reported previously (Ref. 5, and references therein). Triethylamine was added to provide substantial amounts of free secondary (or primary, in case of ω amino acids) amino groups in the reaction system. In the absence of added bases, amino acids do not undergo Michael-type additions to bisacrylamides.[4,5] An excess of bisacrylamide over amino acid was employed, in order to have acrylamido- end groups in the prepolymer.[13] The bis acrylamide–amono acids ratio was chosen in order to have a fairly short poly(amidoamine) chain.

In the second step, N-vinylpyrrolidinone was added to the reaction mixture, and a radical polymerization started by heating at 50°C in presence of 2,2-azo-bis(2-methylpropionitrile) as initiator. The prepolymer itself acted as a crosslinking agent (see Scheme 1). It may be observed that the preceding synthetic route is a quite general one since many other bisacrylamides can be substituted for 1,4-bisacryloylpiperazine, many other ω amino acids or even oligopeptides[4] can be substituted for EDDA, many other vinyl monomers can be substituted for N-vinylpyrrolidinone and, if opportune, alcohols can be substituted for water as reaction solvents. In fact, a great variety of resins can be prepared, and these will be studied for their catalytic activity after Mo(VI) grafting, which in all cases can be performed according to the procedure described in the experimental part.

PRELIMINARY RESULTS ON THE CATALYTIC ACTIVITY

Resin EGDA, after Mo(VI) grafting, was studied as heterogeneous catalyst in both cyclohexene liquid-phase epoxidation, and Baeyer–Villiger oxidation of cyclopentanone to δ-valerolactone. From an analytic and kinetic point of view, the oxygen transfer reactions to olefins can be followed more thoroughly. Concentration–time data for a typical run in ethylbenzene at 80°C obtained with the experimental procedure previously described[9,12] in the presence of EGDA–Mo(VI), heterogeneous B(III)–Mo(VI), and conventional homogeneous $MoO_2(acac)_2$ catalysts are plotted in the Figure 1. The results seem to indicate that under the reported conditions, EGDA catalysts are superior in terms of final yield of epoxide to both heterogeneous B(III)–Mo(VI) catalysts and $MoO_2(acac)_2$, having over the latter the obvious advantage of being heterogeneous.

However, in the presence of EGDA catalysts, an adequate description of the kinetic curves cannot be obtained using our modified Michaelis–Menten model equation
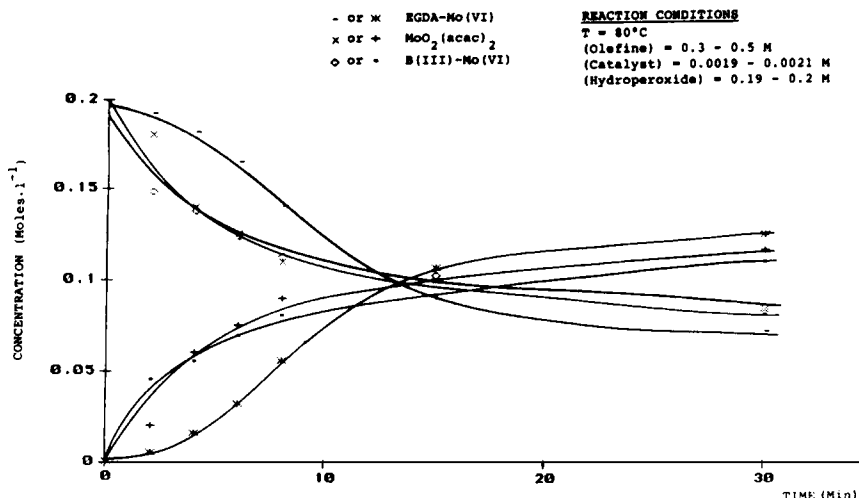
$$X \quad CH_2=CH-C-N \underset{\text{O}}{\overset{\text{O}}{\bigcirc}} N-C-CH=CH_2 \quad + \quad 0.7 \ X \quad \underset{\substack{CH_2 \\ | \\ COOH}}{H-N-CH_2-CH_2-NH} \quad + \quad 0.7 \ X \ (C_2H_5)_3 N$$

$$\xrightarrow{H_2O, \text{ room } t°, \ 24 \text{ hrs}}$$

Scheme text (structures):

$$\bar{n} = \sim 1.7$$

$$+ \ CH_2=CH-N \underset{\text{O}}{\bigcirc} \quad + \ AIBN$$

$$\xrightarrow{50°C}$$

Crosslinked resin

Scheme 1.

Fig. 1.   Variation in the concentration of reactants (hydroperoxide) and products (epoxide) during epoxidation of cyclohexene.

$$r = k \cdot K_S[RO_2H][ol][MeL]$$

where

$$[MeL] = [MeLo] - K_S[MeL][RO_2H] - \left[1 - \frac{k_{i,al}}{K_{i,al}}\right]\int_0^t k_{i,al}[MeL][ROH]^{1/2}dt$$

$$- \left[1 - \frac{k_{i,ep}}{K_{i,ep}}\right]\int_0^t k_{i,ep}[MeL][epox]^{1/2}dt$$

In this equation, which successfully fitted our previous experimental data,[9,12] K_S is the equilibrium constant of the catalyst–hydroperoxide complex while $k_{i,al}$, $k_{i,ep}$, and $K_{i,al}$, $K_{i,ep}$ are the direct rate constants and equilibrium constants of formation of the inhibiting complexes between the catalyst and the alcohol and epoxide, respectively.

The inadequacy of the cited equation in fitting the experimental data obtained in the presence of EGDA catalysts may be due to the absence of kinetic parameters that account for an apparent (see Fig. 1) initial induction period. Under the same conditions, resins similar to EDGA but containing units deriving from monocarboxylic ω amino acid such as glycine, β-alanine, ε-aminocaproic acid, and the like, seem to possess a vastly inferior catalytic activity. Whether or not this is due to the effect of the peculiar structure of ethylendiaminodiacetic acid units, with two carboxyl- and two amino groups in close proximity, and possibly able to cooperate in Mo(VI) grafting, is still open to question, and is presently under investigation.

References

1. N. Indictor and W. Brill, *J. Org. Chem.*, **30**, 2074 (1975).
2. R. A. Sheldon and J. A. Van Doorn, *J. Catal.*, **31**, 427 (1973).
3. S. Ivanov, R. Boeva, and S. Tanielyan, *J. Catal.*, **56**, 150 (1979).
4. F. Danusso and P. Ferruti, *Polymers*, **11**, 88 (1970).
5. P. Ferruti and R. Barbucci, *Adv. Polym. Sci.*, **58**, 57 (1984).
6. P. Ferruti, C. Bertoglio Riolo, T. Soldi, M. Pesavento, and R. Barbucci, *J. Appl. Polym. Sci.*, **27**, 2239 (1982).
7. M. Pesavento, T. Soldi, P. Ferruti, and R. Barbucci, *J. Appl. Polym. Sci.*, **28**, 3361 (1983).
8. P. Ferruti, *Macromolecular Synthes.*, **9**, 25 (1985).

9. E. Tempesti, L. Giuffré, F. Di Renzo, C. Mazzocchia, and G. Airoldi, *Appl. Cataly.*, **26**, 285 (1986).

10. A. J. Durbetaki, *Anal. Chem.*, **28**(12), 2000 (1956).

11. E. St. Jacobson, R. Tang, and F. Mares, *J. C. S. Chem. Comm.*, 888 (1978).

12. E. Tempesti, L. Giuffré, F. Di Renzo, C. Mazzocchia, and G. Modica, *J. Mol. Cataly.*, **45**, 255 (1988).

13. P. Ferruti, D. Arnoldi, M. A. Marchisio, E. Martuscelli, F. Palma, F. Riva, and L. Provenzale, *J. Polym. Sci. Chem.*, **15**, 2151 (1977).

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