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# Copolymerization of $\alpha$-methylstyrene with 4′-*N*-(benzo-15-crown-5)maleimide

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## Summary

4'-N-(Benzo-15-crown-5)maleimide (I) was prepared by dehydration of the corresponding maleamic acid (IV). The complexation constant, K=0.07 L mol$^{-1}$, between I and $\alpha$-methylstyrene ($\alpha$-MeSt) was determined by modified Benesi-Hildebrand NMR method. The copolymerization of $\alpha$-MeSt with homopolymerizable I at different monomer-to-monomer ratios in the feed was performed up to high conversion in Calvet microcalorimeter. It was found that in the copolymerization of $\alpha$-MeSt with an excess of I, the alternating copolymerization precedes the homopolymerization. The mixture of alternating copolymer and homopolymer of I has a single Tg, thus indicating the miscibility on molecular level.

## Introduction

In the free radical initiated copolymerization of $\alpha$-methylstyrene ($\alpha$-MeSt) with maleimide (1,2), N-phenylmaleimide (3,4), N-methylmaleimide (4,5), and a series of N-alkylmaleimides (6,7) (RMI: R = Et, n-Pr, iso-Pr, n-Bu, tert-Bu, n-Hex) it was found that a strong tendency to alternation exists under the different monomer-to-monomer ratios in the feed. It was further found that $\alpha$-MeSt forms with RMI charge-transfer complexes with low complexation constants: $\alpha$-MeSt/RMI, K mol L$^{-1}$: Ph, 0.02; Me, 0.02; Et, 0.05; n-Pr, 0.03; iso-Pr, 0.03; n-Bu, 0.06; n-Hex, 0.06. Similarly, it was found in this work that complexation constant of $\alpha$-MeSt with 4'-N-(benzo-15-crown-5)maleimide (I) is also low and has a value of 0.07 mol L$^{-1}$.

Monomer I was prepared by dehydration of 4'-N-(benzo-15-crown-5)maleamic acid IV obtained by condensation of 4'-amino-benzo-15-crown-5 (III) with maleic anhydride. Amino-crown compound III was prepared by reduction of 4'-nitro-benzo-15-crown-5 (II) with hydrazine hydrate in the presence of Pd/C. The copolymerization of $\alpha$-MeSt with I was performed up to high conversion in CHCl$_3$ in the presence of AIBN as initiator.

## Experimental

### Materials

4'-Aminobenzo-15-crown-5 (III). 4'Nitrobenzo-15-crown-5 (5 g) prepared according to the procedure of Smid et al. (8) [m.p. 98-99°C; lit. 84-85°C (8)] was treated with 20 mL of NH$_2$NH$_2$H$_2$O in the presence of 1.2 g 5% Pd/C following procedure described by Shchori et al. (9) for the preparation of cis-4,4'-diaminobenzo-18-crown-6. Yield 3.8 g (85%) of white crystalline product; m.p. 78-79°C (lit. 73-74°C, prepared by reduction under a H$_2$ pressure of 25-35 psi in the presence of 10% Pd/C, ref.8).

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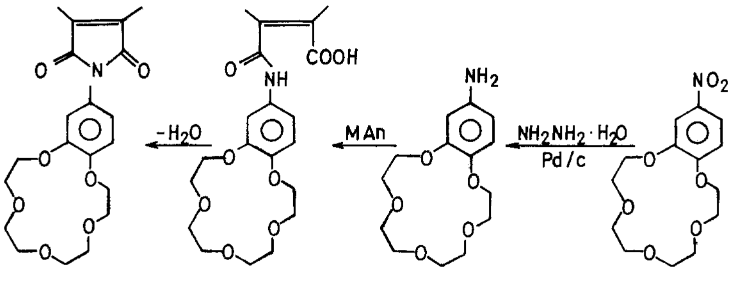

I IV III II

Anal. Calcd. for $C_{14}H_{21}NO_5$ (283.32): C, 59.35; H, 7.47; N, 4.94. Found: C, 60.01; H, 7.92; N, 5.10.

4'-N(Benzo-15-crown-5)maleamic acid (IV). 4'-Aminobenzo-15-crown-5 (III) (2.83 g, 0.01 mol) was dissolved in 20 mL $CHCl_3$ and under vigorous stirring was added dropwise to a solution of 0.98 g (0.01 mol) of maleic anhydride in 20 mL of $CHCl_3$ and left overnight at room temperature. After the removal of $CHCl_3$ in vacuum, the yellow crystalline product was recrystallized from isopropanol yielding 3.8 g (100%) of yellow needles melting at 150-153°C. Analytical sample was recrystallized from ethanol, m.p. 156-158°C.
Anal. Calcd. for $C_{18}H_{23}NO_8$ (381.4): C, 56.68; H, 6.08; N, 3.67. Found: C, 56.32; H, 6.31; N, 3.66.

4'-N-(Benzo-15-crown-5)maleimide (I). Maleamic acid IV (3.25 g) dissolved in 3.5 mL of $Ac_2O$ was heated for 1 hr at 100°C in the presence of 0.35 g of anhydrous sodium acetate. The dark solution was poured into 15 mL of ice-water mixture and stirred for 2 hrs at room temperature. The reaction mixture was extracted with six-100 mL of ether, extract was dried over anhydrous $Na_2SO_4$, ether was evaporated and the crystalline residue (2.67 g) was triturated with 20 mL of cyclohexanone to remove acetic acid. Cyclohexane was decanted and the residue recrystallized from 50 mL of isopropanol yielding 1.45 g of light yellow crystalline product, m.p. 135-140°C. Crystallizetion from benzene yielded 1.2 g (52%) of product with m.p. 148-149°C; m.p. 152°C (DSC).
Anal. Calcd. for $C_{18}H_{21}NO_7$ (363.36): C, 59.49; H, 5.83; N, 3.86. Found: C, 58.92; H, 5.91; N, 3.98.

α-Methylstyrene was commercial product (Aldrich Europe, Belgium) 99% purity which was freshly distilled prior to polymerization.

## Physicochemical measurements

The equilibrium constant of CT-complex of I and α-MeSt was determined by the NMR continuous variation method in $CDCl_3$ at 35°C (10,11). Differential scanning calorimetry was carried out on a Perkin-Elmer, Model DSC-7 using scanning rate of 20°C/min in $N_2$ with a sample size of 15 mg. Thermal stability of copolymer was determined on a TGA V4. OD DuPont 2000 apparatus. Molecular weight was determined on a Varian HPGPC Model 5800 using a set of μ Styragel column with THF as solvent under the callibration with standard polystyrenes of known molecular weights.

## Polymerization procedure

Polymerizations were performed up to high conversion in a differential microcalorimeter Calvet Setaram Instruments, Lyon in $CHCl_3$ at 60°C following procedure previously described (4). The copolymerizations were performed at different monomer-to-monomer ratios in the feed at total monomer concentrations of 0.5 mol $L^{-1}$ and 1 mol $L^{-1}$, respectively. The concentration of AIBN was 0.3 wt%.

## Results and discussion

The association constant of I and α-MeSt complex was determined by the transformed Benesi-Hildebrand NMR method in $CDCl_3$ (10,11). The concentration of I was constant and very small, 0.027 mol $L^{-1}$ so that self association can be neglected, whereas the concentration of α-MeSt varied from 0.37 to 3.0 mol $L^{-1}$. The complexation constant of I and α-MeSt has a value of K=0.07 mol $L^{-1}$ similar to the equilibrium constants of α-MeSt and various N-substituted maleimides, thus indicating that association constants do not depend on steric factors.

The tracings of electromotive force and conversion in the copolymerization of equimolar ratio of α-MeSt with I and in homopolymerization of I are shown in Figure 1.

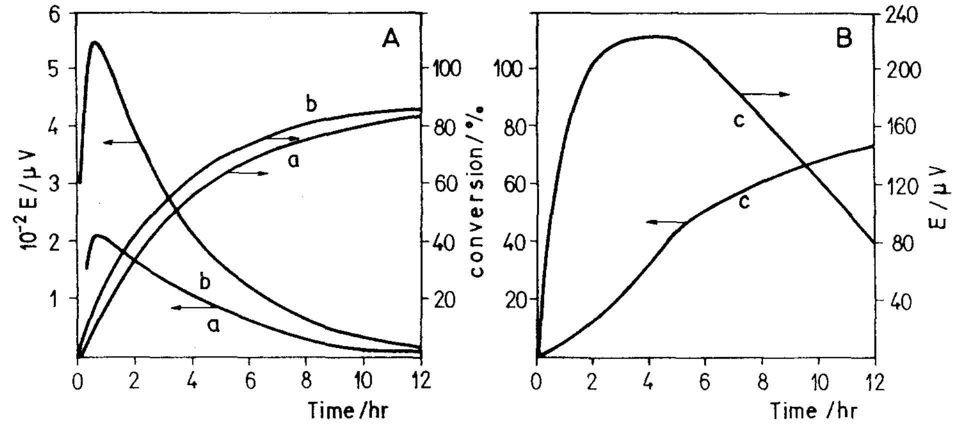

Figure 1. Calvet microcalorimetry tracings and conversions against time in the copolymerization of α-methylstyrene with 4'-N-(benzo-15-crown-5)maleimide (I) at equimolar ratio of comonomers (A) and in homopolymerization of I (B); $CHCl_3$; 0.3 wt% of AIBN at 60°C. Total monomer concentration: a) 0.5 mol $L^{-1}$; b) 1.0 mol $L^{-1}$; c) 1.0 mol $L^{-1}$.

In the previous papers it was found that at high conversion copolymerization of α-MeSt with an excess of homopolymerizable N-substituted maleimides there is a distinct indication of the point where the homopolymerization starts after the alternating copolymerization is completed. In contrast to these findings, the data in Figure 2 show that it is not possible to determine the point where the copolymerization is completed.

In order to get better insight into the mechanism of copolymerization of $\alpha$-MeSt with I in the presence of an excess of homopolymerizable I, the first order rate constants K $min^{-1}$ were determined as slope from the plot of $\ln [M_o]/[M_t]$ against time for alternating copolymerization (Figure 1A) $k_{alt}=0.0035$ $min^{-1}$ (for 0.5 mol $L^{-1}$) and $k_{alt}=0.0046$ $min^{-1}$ (for 1 mol $L^{-1}$) and for homopolymerization (Figure 1, B): $k_{homo}=0.0015$ $min^{-1}$ (for 1 mol $L^{-1}$).

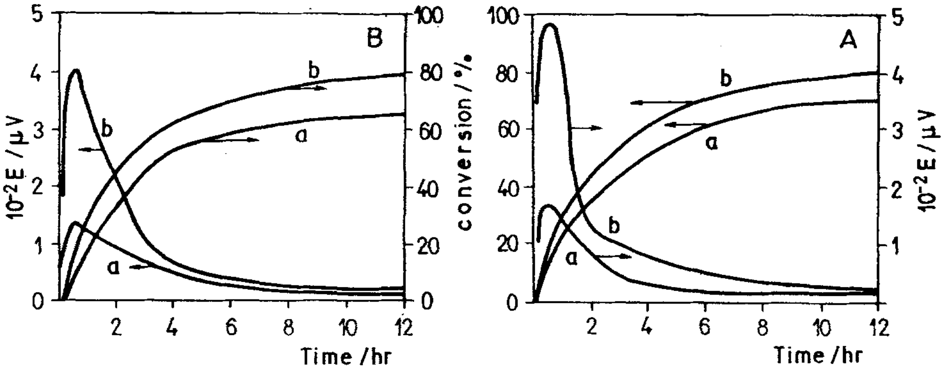

Figure 2. Calvet microcalorimetry tracings and conversions against time in the copolymerization of $\alpha$-methylstyrene with 4'-N-(benzo-15-crown-5)maleimide (I) at molar concentrations of $\alpha$-MeSt to I: A) 0.2 to 0.8 (I); B) 0.3 to 0.7 (I); $CHCl_3$ at 60°C; 0.3 wt% AIBN; total monomer concentrations: a) 0.5 mol $L^{-1}$; b) 1.0 mol $L^{-1}$.

Following the same procedure, the first order rate constants in the copolymerization of $\alpha$-MeSt with an excess of I were determined in the region below the theoretical conversion of alternating copolymerization and above this region. The numerical values of rate constants are shown in Table 1.

Table 1. Rate constants in copolymerization of $\alpha$-methylstyrene with 4'-N-(benzo-15-crown-5)maleimide (I) for alternating copolymerization and homopolymerization of I; monomer concentration 1 mol $L^{-1}$

| Molar ratio $\alpha$-MeSt | I | Theor. alt % | $k_{alt}$ $min^{-1}$ | $k_{homo}$ $min^{-1}$ | |
|---|---|---|---|---|---|
| 0 | 1.0 | - | - | 0.0015 | Fig. 1B |
| 0.5 | 0.5 | 100 | 0.0046 | - | Fig. 1A(b) |
| 0.3 | 0.7 | 49.79 | 0.0057$^{1)}$ | 0.0013$^{2)}$ | Fig. 2B(b) |
| 0.2 | 0.8 | 30.61 | 0.0040$^{3)}$ | 0.0017$^{4)}$ | Fig. 2A(b) |

Conversions between: 1) 0-35%; 2) 52-61%; 3) 0-30%; 4) 38-51%.

The data in Table 1 indicate that there is a good agreement between the rate constants of alternating copolymerization at equimolar ratio of comonomers and the rate constants at the conversion which is below the theoretical conversion of alternating copolymerization at 0.3 to 0.7 and 0.2 to 0.8 molar ratio of comonomers. The same was also found for the homopolymerization in Fig. 1B and Figs. 2A and 2B.

Properties of Polymers. Molecular weight of alternating copolymer $M_w$= 7800; $M_n$=4800; $Tg_{alt}$: 459K $TGA_{alt}$: loss of weight: 1.9% at 280°C; 86.3% at 480°C; residue 9.35% at 599.9°C, midpoint 408.1°C. One Tg is found in the mixture of alternating copolymer with homopolymer of I : alt/homo = 1/1.4, Tg=453K; alt/homo = 1/0.32, Tg=446K. One Tg indicates that alternating copolymer and homopolymer of electron acceptor are miscible on molecular level.

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