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FREE-RADICAL-INITIATED POLYMERIZATION OF 6-MALEIMIDOCHOLESTERYLHEXANOATE AND 4-MALEIMIDOCHOLESTERYLBENZOATE AND COPOLYMERIZATION WITH α -METHYLSTYRENE

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ABSTRACT

Synthesis and free-radical-initiated homopolymerization of 6-maleimidocholesterylhexanoate (MICHHex) and 4-maleimidocholesterylbenzoate (MICHBenz) and copolymerization with α -methylstyrene (α -MeSt) are described. Monomers and α -MeSt form charge-transfer (CT) complexes with equilibrium constants: $K_{\text{MICHHex}/\alpha\text{-MeSt}} = 0.06 \text{ L}\cdot\text{mol}^{-1}$ and $K_{\text{MICHBenz}/\alpha\text{-MeSt}} = 0.05 \text{ L}\cdot\text{mol}^{-1}$. The mechanism based on the participation of CT complex best explains the formation of alternating copolymers. Homopolymers and copolymers are film-forming materials which are stable up to 330°C under the conditions of TGA. T_g s and other thermal transitions are below the decomposition temperature.

INTRODUCTION

During the last few decades a large number of polymers which contain mesogenic groups in the side chains have been synthesized as potential liquid crystalline polymers. Of special interest are polymers based on *N*-substituted maleimides which can be easily synthesized from readily available chemicals, and, what is of importance, they are stable compounds which can easily polymerize and copolymerize with the formation of high molecular weights polymers. The recent papers published

by Oishi [1] and Barrales-Rienda [2] provide lists of references which describe the preparation and properties of side-chain liquid crystalline poly(*N*-substituted maleimides). We recently published a paper on the preparation and properties of poly [*N*-4'-(benzo-15-crown-5)maleimide] and its copolymer with α -methylstyrene [3].

Free-radical-initiated polymerization of *N*-substituted maleimides proceeds predominantly via trans-addition with the formation of comblike polymers. These polymers are characterized by the presence of rigid succinimido groups along the principal polymer chains, which in many cases leads to the formation of regular domains in amorphous polymers [1, 4-6].

N-Substituted maleimides readily homopolymerize and copolymerize with various electron-acceptor monomers. Otsu and coworkers [7] showed that the rate of polymerization of *N*-*tert*-butylmaleimide is higher than the rate of polymerization of other *N*-butylmaleimides in spite of its higher bulkiness. However, in the polymerization of *N*-amylmaleimide and *tert*-octylmaleimide, the same authors showed that the rate of polymerization decreases with an increase of bulkiness of the *N*-substituent [8].

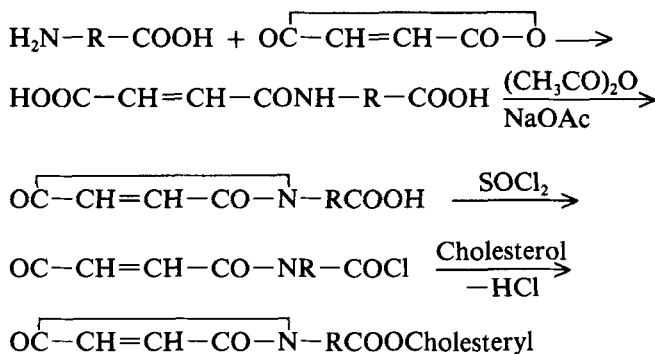
It is further of interest to mention that in the copolymerization of *N*-alkylmaleimides RMI (R = Me, Et, *n*-Pr, *iso*-Pr, *tert*-Bu, *n*-Hex) with α -methylstyrene, the rate of polymerization decreases with an increase in the bulkiness of alkyl groups [9, 10]. During the course of our studies on the copolymerization of α -methylstyrene with *N*-methylmaleimide [11] and *N*-(benzo-15-crown-5)maleimide [3], it was found that copolymerization proceeds under the participation of charge-transfer (CT) complexes, yielding alternating copolymers with α -methylstyrene.

In the present paper we report our work on the synthesis of maleimidocholesterylhexanoate (MICHex) and maleimidocholesterylbenzoate (MICHenz) as monomers used in the preparation of homopolymers and copolymers with α -methylstyrene. The mechanism of polymerization and copolymerization in the presence of AIBN and the properties of the polymers are also described.

EXPERIMENTAL

Physicochemical Measurements

NMR spectra were obtained on a Varian EM 390 spectrometer. The copolymer composition was determined by NMR spectrometry and by elemental analysis. The equilibrium constants of CT complexation were determined by the NMR continuous variation method in deuterated chloroform at 35°C [12, 13]. Differential scanning calorimetry was carried out on a Perkin-Elmer model DSC-2 with a scanning rate of 20°C·min⁻¹ in nitrogen with a sample size of 10-20 mg. The glass transition temperature was taken as the half-height of the corresponding heat capacity jump. The other transition temperatures were measured at the maximum of the peak. Thermogravimetric analysis was carried out on a Perkin-Elmer TGS-2 Thermogravimetric System in a nitrogen stream at a heating rate of 10°C·min⁻¹. The average molecular weights were determined by the GPC at room temperature in THF (Varian HPGPC model 8500) with PS standards.



SCHEME 1. Synthesis of maleimidocholesterylhexanoate [$\text{R} = -(\text{CH}_2)_5-$] and maleimidocholesterylbenzoate ($\text{R} = \text{C}_6\text{H}_5$).

Preparation of Monomers

The synthetic procedure for monomers MICHex and MICHenz are presented in Scheme 1.

6-Hexanoylmaleamic Acid

6-Aminohexanoic acid (19.6 g, 0.15 mol) was dissolved in 70 mL acetic acid and mixed with a solution of 14.7 g (0.15 mol) maleic anhydride in 70 mL acetic acid. The mixture was stirred at room temperature for 3.5 hours. The white precipitate was filtered off and dried in vacuum at 70°C, yielding 33.17 g (96.5%) of a white crystalline product, mp 167°C.

Analysis. Calculated for $\text{C}_{10}\text{H}_{15}\text{NO}_5$ (%): C, 52.39; H, 6.55; N, 6.11. Found (%): C, 52.95; H, 6.94; N, 7.23.

6-Maleimido Hexanoic Acid

A mixture of 33 g (0.14 mol) of 6-hexanoylmaleamic acid, 2 g anhydrous Na-acetate, and 23 mL acetic acid anhydride was heated for 30 minutes in a water bath. The dark solution was cooled, poured into 200 mL iced water, and stirred for 2 hours. The reaction mixture was extracted with ether, and the ether layer was dried with Na_2SO_4 . Evaporation of ether gave 23.2 g of crude 6-maleimido hexanoic acid. The crude acid was treated with a saturated NaHCO_3 solution, the aqueous solution was extracted with ether, and then acidified with dilute hydrochloric acid. The precipitate was extracted with ether, the organic layer was dried with anhydrous MgSO_4 , and the ether was evaporated in vacuum. The yield was 13 g (43%) of pure maleimid melting at 75–76°C.

Analysis. Calculated for $\text{C}_{10}\text{H}_{13}\text{NO}_4$ (%): C, 56.86; H, 6.20; N, 6.63. Found (%): C, 57.22; H, 6.68; N, 6.89.

6-Maleimidohexanoyl Chloride

6-Maleimidohexanoic acid (5.68 g) was refluxed for 2 hours with 30 mL thionyl chloride. Thionyl chloride was evaporated in vacuum, and the dark oily residue was distilled at 104°C under a pressure of 10^{-3} mmHg. The yield was 4.3 g (70.1%) of a semicrystalline product.

Analysis. Calculated for $C_{10}H_{12}NO_3Cl$ (%): C, 52.28; H, 5.26; N, 6.10. Found (%): C, 49.05; H, 5.07; N, 7.59.

6-Maleimidocholesterylhexanoate (MICHex)

A solution of 4.3 g (0.019 mol) maleimidohexanoyl chloride and 7.25 g (0.019 mol) cholesterol in 180 mL benzene was refluxed for 48 hours. Benzene was evaporated in vacuum, and the oily residue was triturated with 50 mL ether under reflux. The insoluble part was removed by filtration and discarded, while the residue obtained upon the evaporation of ether was dissolved in 200 mL petrolether (bp 30–60°C) and left in a refrigerator overnight. The crystalline product was removed by suction filtration, yielding 7.76 g pure ester, mp 95–96°C. Partial evaporation of the mother liquor gave an additional 1.3 g MICHex. Total yield: 9.06 g (83%).

Analysis. Calculated for $C_{37}H_{58}NO_4$ (%): C, 76.51; H, 10.06; N, 2.41. Found (%): C, 75.97; H, 10.30; N, 2.35.

4-Maleimidobenzoyl Chloride

4-Maleimidobenzoic acid [14] (7 g) was refluxed for 2 hours with 30 mL thionyl chloride. Thionyl chloride was removed in vacuum, yielding 7.5 g crude acid chloride. Recrystallization from 50 mL benzene and 10 mL petrolether (bp 30–60°C) gave 6.2 g (80.9%) of a yellow crystalline product. At 160°C the chloride sublimes in the form of fine needles which sharply melt at 167–168°C.

Analysis. Calculated for $C_{11}H_6NO_3Cl$ (%): N, 8.33. Found (%): N, 8.15.

4-Maleimidocholesterylbenzoate (MICHBenz)

A mixture of 1.88 g (0.008 mol) 4-maleimidobenzoyl chloride and 3.09 g (0.008 mol) cholesterol was placed into a round-bottomed flask, dissolved in benzene, and then the flask was connected to a water jet pump. Benzene was evaporated, and the dry residue was heated in an oil bath to 150°C for 20 minutes when the evolution of HCl ceased. In order to prevent excessive foaming, air was introduced into the flask from time-to-time. The oily residue was dissolved in benzene, and in order to remove traces of HCl, the benzene was evaporated in vacuum. The oily residue was triturated with 30 mL ether, cooled overnight in a refrigerator, and the white crystalline product was filtered off and used without further purification in the polymerization reaction. Yield: 4.21 g (80.5%); mp 166–170°C.

Analysis. Calculated for $C_{38}H_{51}NO_4$ (%): C, 77.91; H, 8.77; N, 2.39. Found (%): C, 77.69; H, 8.76; N, 2.47.

Polymerization Procedure

Polymerization was performed in vacuum-sealed 10-mL glass vials which were thoroughly degassed, filled with nitrogen before sealing, and placed into an oil bath thermostated at 60°C. Polymerization was performed in toluene with 0.3 wt% AIBN. The viscous solutions of polymers were diluted with solvent and precipitated by the dropwise addition of methanol. The precipitated polymers were filtered off and dried in vacuum at 70°C overnight.

RESULTS AND DISCUSSION

The data in Scheme 1 indicate that the preparation of monomers MIChHex and MIChBenz follows simple reactions, and although the yields are not optimized, they are relatively high. Both monomers homopolymerize in the presence of AIBN in the same manner as other *N*-substituted maleimides. A comparison of the rate of conversion of MIChBenz and *N*-phenylmaleimide (NPhMI) is shown in Fig. 1, and it indicates that the rates of homopolymerization of MIChBenz and NPhMI [15] are not significantly different in spite of the difference in the bulkiness of the *N*-substituents.

In the homopolymerization of MIChHex which has a flexible spacer between maleimido and the cholesteryl group, a conversion of 81% was reached after 8 hours. Homopolymers poly-MICHBenz and poly-MICHHex are thermally stable, film-forming materials of relatively high molecular weights, as indicated in Table 1.

In our previous studies it was shown that *N*-substituted maleimides form CT complexes with α -MeSt with low complexation constants. However, in all the copolymerization reactions studied, one-to-one copolymers were obtained [16]. By applying the NMR continuous variation method it was found that the equilibrium constants of MIChHex and MIChBenz with α -MeSt are also relatively low: $K_{\text{MIChHex}/\alpha\text{-MeSt}} = 0.06 \text{ L} \cdot \text{mol}^{-1}$, $K_{\text{MIChBenz}/\alpha\text{-MeSt}} = 0.05 \text{ L} \cdot \text{mol}^{-1}$. As expected, both

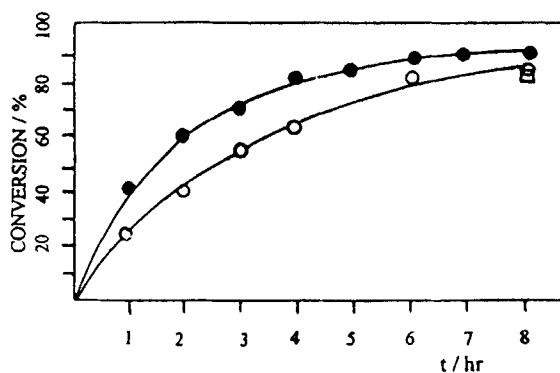


FIG. 1. Comparison of the rates of conversion in the homopolymerization of 4-maleimidocholesterylbenzoate (●), *N*-phenylmaleimide (○) [15], and 6-maleimidocholesterylhexanoate (□); 0.3 wt% AIBN in toluene at 60°C.

TABLE 1. Polymerization Conditions and Properties of Poly-MICHHex, Poly-MICHBenz, Poly(MICHHex-*alt*- α -MeSt), and Poly(MICHBenz-*alt*- α -MeSt); 0.3 wt% AIBN in Toluene at 70°C

Polymer	Monomer in feed, mol·L ⁻¹	Conversion % in 8 hours	RMI: α -MeSt in copolymer	10 ⁻³ Molecular weights		Analysis, %			
				\bar{M}_w	\bar{M}_n	Found	Theoretical		
Poly-MICHHex	0.5	81	—	20.5	12.8	C	74.57	C	76.51
						H	10.30	H	10.06
						N	2.35	N	2.41
Poly-MICHBenz	0.5	84	—	53.5	23.7	C	77.69	C	77.91
						H	8.76	H	8.77
						N	2.47	N	2.39
Poly(MICHHex- <i>alt</i> - α -MeSt)	0.8 ^a	70	1:1 ^b	94.5	50.5	C	78.21	C	79.03
						H	9.71	H	9.80
						N	3.13	N	2.00
Poly(MICHBenz- <i>alt</i> - α -MeSt)	0.8 ^a	86	1:1 ^b	49.3	60.1	C	80.33	C	80.20
						H	8.66	H	8.68
						N	2.29	N	1.99

^aRMI: α -MeSt in feed 1:1.

^bBy NMR spectrometry.

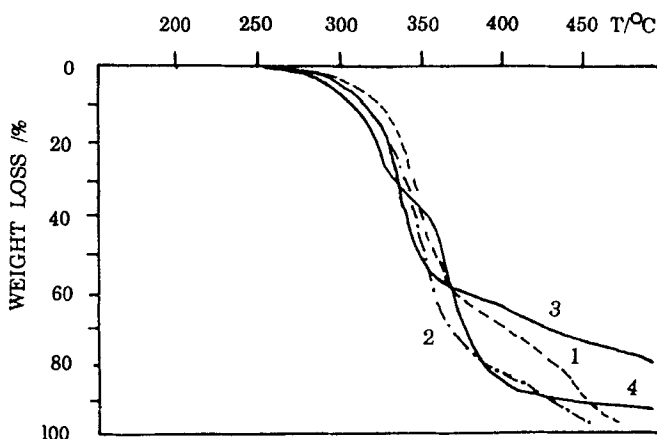


FIG. 2. Thermogravimetric analysis of 1) poly-MICHex; 2) poly(MICHex-*alt*- α -MeSt); 3) poly-MICHBenz; 4) poly(MICHBenz-*alt*- α -MeSt) in N_2 ; heating rate $10^\circ C \cdot min^{-1}$.

cholesteryl esters give alternating copolymers with α -MeSt in high conversion copolymerization (Table 1). It was further found that in the copolymerization of homopolymerizable MICHBenz and MICHHex with α -MeSt at a molar ratio in the feed of 0.3/0.7, the alternating copolymers were obtained in almost the theoretically possible yields (94% for MICHBenz and 96% for MICHHex). This indicates that the mechanism of copolymerization of MICHHex and MICHBenz with α -MeSt is the same as the one previously described in the copolymerization of RMI with α -MeSt [16].

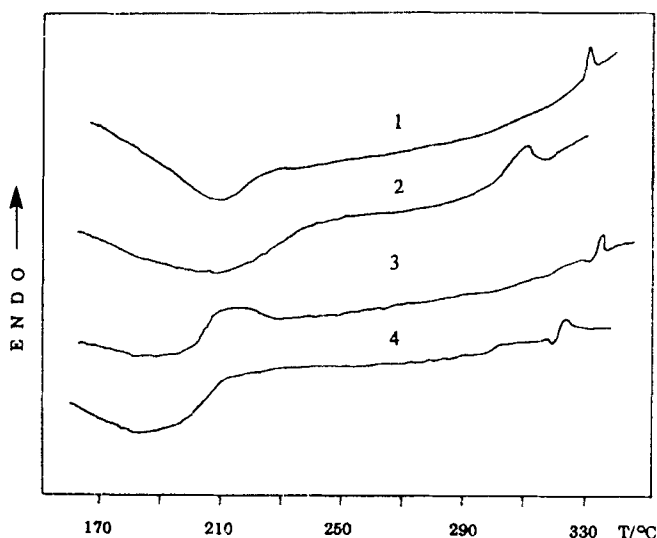


FIG. 3. DSC thermograms of 1) poly-MICHex; 2) poly(MICHex-*alt*- α -MeSt); 3) poly-MICHBenz; 4) poly(MICHBenz-*alt*- α -MeSt); scanning rate $20^\circ C \cdot min^{-1}$ in nitrogen; second scan.

TABLE 2. Thermal Properties of Poly-MIChHex, Poly-MIChBenz, and Copolymers with α -MeSt

Polymer	T_g , °C	T_{trans} , °C ^a	Weight loss, °C		
			10%	25%	50%
Poly-MIChHex	201	331	325	340	355
Poly-MIChBenz	215	327	325	332	350
Poly(MIChHex- <i>alt</i> - α -MeSt)	200	321	325	340	355
Poly(MIChBenz- <i>alt</i> - α -MeSt)	223	308	325	340	365

^a T_{trans} is the transition temperature above T_g .

The polymers and copolymers prepared for this paper are thermally stable materials which in TGA experiments rapidly decompose between 300 and 400°C by a rather complicated mechanism (Fig. 2). It is also evident that the weight loss for all four polymers is about 10% at 330°C.

Transition temperatures of the prepared homopolymers and alternating copolymers were determined by DSC at a scan rate of 20°C·min⁻¹. The DSC tracings and numerical values are presented in Fig. 3 and Table 2, and they indicate that the T_g s of polymers which contain a flexible spacer are 10–20°C lower than those of benzoic acid esters. On the other hand, the transitions at higher temperatures (T_{trans}) are 5–10°C lower for polymers which contain a rigid aromatic ring in the side chains.

CONCLUSION

1. Cholesteryl esters of maleimidohexanoic acid and maleimidobenzoic acid were prepared by cyclization of the corresponding maleamic acids followed by esterification with cholesterol.
2. The free-radical-initiated polymerization of MIChHex and MIChBenz and copolymerization with α -MeSt gave homopolymers and alternating copolymers with high molecular weights.
3. The alternating copolymerization of MIChHex and MIChBenz with α -MeSt proceeds with the participation of CT complexes.
4. The homopolymers and copolymers are film-forming materials stable up to 330°C. The transition temperatures are within the thermally stable region in all cases.

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