New basic multifunctional polymers: 5. Poly(esterthioetheramine)s by polyaddition of 2,2′-alkylenediimino diethanethiols to bisacrylic and bismethacrylic esters

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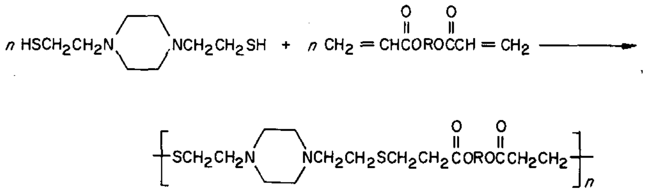
New tertiary amino polymers having the structure of poly(esterthioetheramine)s have been prepared by polyaddition of 2,2′-alkylenediiminodiethanethiols to bisacrylic esters and bismethacrylic esters. Kinetic measurements performed on polymerization rate show that the latter are less reactive towards polyaddition reaction. Moreover the presence of protogenic substances in the reaction medium considerably enhances the polyaddition rate.

(Keywords: poly(aminoester)s; aminothiols; polymeric amines; bisacrylic esters; bismethacrylic esters; polyaddition)

INTRODUCTION

In recent papers, we have reported our results on some new families of tertiary amino polymers obtained from 2,2′-alkylenediiminodiethanethiols by either polyoxidative coupling[1], or Michael-type polyaddition to compounds bearing activated double bonds[2–4]. This is part of wider research on synthesis, properties and biomedical applications of multifunctional macromolecules[5,6]. In particular, several examples of poly(esterthioetheramine)s have been described in a preliminary letter[2]. These were obtained by polyaddition of 2,2′-(1,4-piperazinediyl)diethanethiol (**I**) to bisacrylic esters:



In this paper we report the results of a further study on the polyaddition of **I** and other monomers of similar structure to both bisacrylic and bismethacrylic esters, with the aim of reaching a better knowledge in this field and widening the scope of this polymerization reaction.

EXPERIMENTAL

Measurements

Intrinsic viscosities were measured in $CHCl_3$ at 30°C with an Ubbelohde viscometer, and determined according to the method of Solomon and Ciuta[7]. Molecular weight measurements were performed in $CHCl_3$ at 30°C with a Perkin Elmer Model 115 vapour pressure osmometer. ^1H n.m.r. spectra were run at 80 MHz on an EM 360A Varian spectrometer in $CDCl_3$, using tetramethylsilane (TMS) as internal reference.

Monomers

Monomer I and 3,6-dimethyl-3,6-diazaoctane-1,8-dithiol (**II**) were prepared by ring opening addition of ethylene sulphide to the corresponding amines, as previously described[1,4]. They were distilled under reduced pressure just before use. 1,6-Hexamethylenediacrylate (**III**) and ethylene dimethacrylate (**IV**) (Aldrich, Germany) were purified by vacuum distillation. 1,4-Phenylene diacrylate and 1,4-phenylene dimethacrylate were prepared as previously described[8] and recrystallized just before use.

Polymers

Polymers **V**–**XI** were synthesized according to the following procedure. Equimolecular quantities of bisthiol and bisacrylic or bismethacrylic esters, tertbutyl alcohol (the same weight as the vinyl ester) and dry toluene (about two volumes with respect to the combined volumes of the monomers) were mixed in a glass ampoule and then carefully degassed and placed under nitrogen. The reaction mixtures were maintained under nitrogen at constant temperature (30 ± 1°C) for 5 days, in the case of bisacrylates, and 10 days in the case of bismethacrylates, then evaporated to dryness *in vacuo*, the residue extracted with n-hexane, and finally dried to constant weight at 0.1 mbar.

The reaction mixtures were homogeneous until the end in all cases except for polymers **VII** and **XI**, which partly separated in a highly swollen state after a few hours. The n-hexane extraction was omitted in the cases of polymers

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V and **VIII**, which appeared to be partly soluble in this solvent in the presence of residual traces of toluene. The yields were always high (75–85%). The polymers may absorb CO_2 and for analytical purposes should be stored in closed vessels and in the presence of KOH pellets. All polymers were individually characterized: the main analytical data are as follows.

Polymer V. ^{1}H n.m.r. ($CDCl_3$): $\delta = 1.25$ (m; 16H, NC–$(CH_2)_4$–CN and COOC$(CH_2)_4$COOC), 4.5 (m; 4H, $COOCH_2$) and 2.1–3.3 (m; 26H, all other H).
$(C_{24}H_{46}N_2O_4S_2)_n$ $(490.77)_n$. Calculated: C 58.74; H 9.45; N 5.71; S 13.07. Found: C 58.45; H 9.50; N 5.68; S 13.13.

Polymer VI. ^{1}H n.m.r. ($CDCl_3$): $\delta = 1.25$ (m; 8H, NC$(CH_2)_4$CN), 7.45 (s; 4H, aromatic CH=) and 2.1–3.3 (m; 18H, all other H).
$(C_{24}H_{38}N_2O_4S_2)_n$ $(482.70)_n$. Calculated: C 59.72; H 7.94; N 5.80; S 13.28. Found: C 59.61; H 7.98; N 5.77; S 13.40.

Polymer VII. ^{1}H n.m.r. ($CDCl_3$): $\delta = 1.25$ (m; 8H, NC$(CH_2)_4$CN), 4.45 (m; 4H, $COOCH_2$) and 2.2–3.3 (m; 24H, all other H).
$(C_{20}H_{36}N_2O_4S_2)_n$ $(432.35)_n$. Calculated: C 59.72; H 7.94; N 5.80; S 13.28. Found: C 59.61; H 7.98; N 5.77; S 13.40.

Polymer VIII. ^{1}H n.m.r. ($CDCl_3$): $\delta = 1.2–1.5$ (m; 14H, NC$(CH_2)_4$CN and CH_3C), 4.5 (m; 4H, $COOCH_2$) and 2.2–4.5 (m; 24H, all other H).
$(C_{24}H_{42}N_2O_4S_2)_n$ $(486.74)_n$. Calculated: C 66.63; H 9.78; N 6.47; S 14.82. Found: C 66.10; H 9.83; N 6.43; S 14.91.

Polymer IX. ^{1}H n.m.r. ($CDCl_3$): $\delta = 1.25–2.5$ (m; 14H, NC$(CH_2)_4$CN, 7.45 (s; 4H, aromatic CH=) and 2.1–3.2 (m; 24H, all other H).
$(C_{26}H_{42}N_2O_4S_2)_n$ $(510.76)_n$. Calculated: C 61.14; H 8.29; N 5.48; S 12.53. Found: C 60.89; H 8.31; N 5.51; S 12.42.

Polymer X. ^{1}H n.m.r. $(CDCl_3)_n$: $\delta = 1.25$ (s; 6H, CH_3C), 4.5 (m; 4H, $COOCH_2$) and 2.2–3.2 (m; 22H, all other H).
$(C_{18}H_{32}N_2O_4S_2)_n$ $(404.60)_n$. Calculated: C 53.43;H 7.97; N 6.92; S 15.85. Found: C 54.23; H 8.10; N 6.82; S 15.66.

Polymer **XI**. ^{1}H n.m.r. ($CDCl_3$): $\delta = 1.25$ (s; 6H, CH_3C), 4.5 (m; 4H, $COOCH_2$) and 2.2–3.3 (m; 22H, all other H).
$(C_{22}H_{32}N_2O_2S_2)_n$ $(452.62)_n$. Calculated: C 58.38; H 7.13; N 6.19; S 14.17. Found: C 57.91; H 7.19; N 6.17; S 14.08).

Kinetic measurements

The polyaddition reactions of monomer **I** to monomer **III** and **IV** respectively were followed via ^{1}H n.m.r. spectroscopy, by monitoring the decrease of the integrals relative to the area of acrylic or methacrylic peaks. The reaction mixtures were sealed into ^{1}H n.m.r. tubes to prevent evaporation of solvent and oxidation of the thiol group, and maintained at constant temperature in a thermostatic bath. In all cases a total amount of 1 ml solution was employed. Kinetic measurements were performed by putting the tubes into the n.m.r. probe at regular time intervals and sweeping the integrals in the chemical shift range of interest (4–6 ppm). Concentrations of reagents ranged from 0.4 to 1.0 M for the vinyl ester and mercapto compound and from 1.0 to 2.0 M for tertbutyl alcohol. Reaction temperature was maintained at 30°C and 45°C, respectively, for different sets of experiments. C_6D_6 was selected as aromatic solvent.

RESULTS AND DISCUSSION

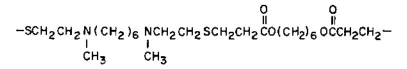
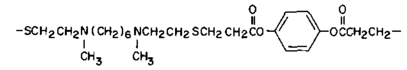
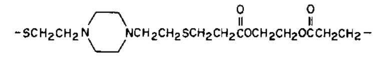
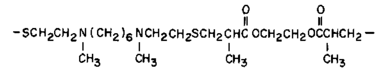
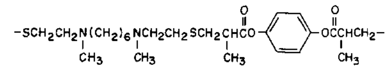
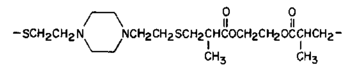
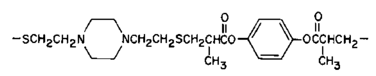
Polymerization

The Michael-type polyaddition of 2,2-'alkylenediiminodiethanethiols to bisacrylic or bismethacrylic esters proved to be an easy and convenient method for the synthesis of tertiary amino polymers. The reaction takes place smoothly in organic solvents at moderate temperatures and without added catalysts. It is known[9,10] that polymers are obtained by polyaddition of bisthiols to bisacrylic or methacrylic esters in the presence of basic catalysts. In our case, it is apparent that the mercaptoamines act both as monomers and catalysts. The new polymeric substances prepared are reported in *Table 1*, together with some characterizations. Most of the polymers, when isolated, are amorphous gums or viscous liquids. However, the polymer derived from the aromatic bisacrylic ester (**VI**) gradually turns into a white solid on standing at room temperature. All the polymers reported in this paper are soluble in most organic solvents and in aqueous media at pH ⩽ 5. It may be noticed that the number average molecular weights of polymers **V**–**XI** are rather low, ranging from 4000 to 9000, although the polyaddition reactions could be pushed to high conversions in the selected reaction time. This might be due to side reactions occurring during the polymerization process, such as cyclization or transesterification reactions, but we have no experimental data, at present, to elucidate this point.

Kinetic measurements

It was thought worthwhile to study in some detail the polymerization kinetics of two selected pairs of monomers, **I**–**III** and **I**–**IV**, in order to compare the behaviour of a diacrylate and a dimethacrylate of similar structure. Moreover, since there have been some arguments about the convenience of using solvents with mobile protons in Michael-type polyadditions of some bisthiols to compounds with activated double bonds[10], we have performed kinetic experiments, both in an aprotic medium (pure benzene), and in a polymerization medium containing, besides benzene, a protogenic substance (tertbutyl alcohol). We chose a tertiary alcohol as proton donor to prevent possible transesterification reactions with ester groups. Kinetic experiments were performed following the reaction progress via ^{1}H n.m.r. spectroscopy (see Experimental section). A typical conversion curve is shown in *Figure 1*. The reaction rates of methacrylates are lower, as apparent from a comparison of the kinetic curves. This is probably due to the steric hindrance in the proximity of the reactive site, and to the +I effect of the methyl substituent. In all cases, the addition of a protogenic substance greatly enhances the polymerization rate.

Table 1 Structures of new poly(esterthioetheramine)s

N_0	Structure of the repeating unit	$\bar{M}_n$[a]	$[\eta]$[b]	Solubility[c]
V	 $-SCH_2CH_2\underset{CH_3}{N}(CH_2)_6\underset{CH_3}{N}CH_2CH_2SCH_2CH_2\overset{O}{\overset{\Vert}{C}}O(CH_2)_6O\overset{O}{\overset{\Vert}{C}}CH_2CH_2-$	5100	0.35	B,C,E,L,N,O,P
VI		4300	0.30	B,C,E,L,N,O,P
VII		8400	0.50	B,C,E,L,N,O,P
VIII	 $-SCH_2CH_2\underset{CH_3}{N}(CH_2)_6\underset{CH_3}{N}CH_2CH_2SCH_2\underset{CH_3}{C}H\overset{O}{\overset{\Vert}{C}}OCH_2CH_2O\overset{O}{\overset{\Vert}{C}}\underset{CH_3}{C}HCH_2-$	4600	0.31	B,C,E,F,H,L,N,O,P
IX		5200	0.38	B,C,E,L,N,O,P
X		4100	0.33	B,C,E,L,N,O,P
XI		4000	0.31	B,C,E,O,P

[a] Number average molecular weight from osmometric measurements in chloroform
[b] Intrinsic viscosity in chloroform at 30°C (dl g^{-1})
[c] Solvents tried: A, water; B, 0.1 M HCl; C, acetate buffer pH 4.68; D, phosphate buffer pH 6.88; E, chloroform; F, methanol; G, isopropanol; H, ethyl ether; I, acetone; L, ethyl acetate; M, n-heptane; N, toluene; O, dimethylsulphoxide; P, dimethylformamide

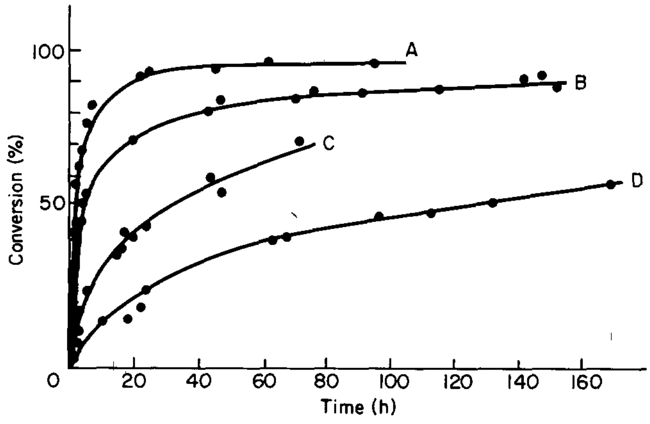


Figure 1 Polyaddition of monomer I to monomer III (curves A and B), and to monomer IV (curves C and D). Experimental conditions: curves A and C: $[V]=[T]=0.80$ M; curves B and D: $[V]=[T]=0.94$ M; $[A]=2.12$ M; temperature = 30°C

This led us to consider that 2,2′-alkylenediiminodiethanethiols, besides being reagents, act both as self catalysts and proton donors. We therefore elaborated our experimental data according to the following kinetic patterns:

$$-\frac{d[V]}{dt}=k_1[V][T] \quad (1)$$

$$-\frac{d[V]}{dt}=k_2[V][T]^2 \quad (2)$$

$$-\frac{d[V]}{dt}=k_2[V][T]^2+k_3[V][T][A] \quad (3)$$

where $[V]$ = vinyl ester concentration, $[T]$ = thiol concentration, $[A]$ = alcohol concentration, k_1 = kinetic constant relative to ester–thiol reaction, k_2 = kinetic constant containing parameters relative to mercapto group acid catalysis and k_3 = kinetic constant containing parameters relative to alcoholic group acid catalysis.

Equations (1) and (2) were tested in the absence of tertbutyl alcohol. With $[V_0]=[T_0]$, after integration of equations (1) and (2) the following relationships result:

$$\frac{[V_0]}{[V]}=1+k_1[V_0]t \quad (4)$$

$$\left(\frac{V_0}{[V]}\right)^2=1+2k_2[V_0]^2t \quad (5)$$

Equation (4) did not fit experimental data and therefore mathematical model (1) was excluded. On the contrary equation (5) proved to be in reasonable agreement with the experimental data, since plotting $(V_0/V)^2$ *versus* time, a straight line is obtained, whose slope is related to k_2. Equation (3) was tested in the presence of tertbutyl alcohol. The differential equation was solved into the unknown k_3 by means of a numerical integration technique. Values of k_2 obtained from kinetics carried out in pure benzene were employed, while starting values of k_3 parameter were determined using an approximate solution of equation (3). Kinetic constants, relative to addition reaction both to acrylic and methacrylic monomer, were obtained as the average of several kinetic measurements, conducted at different concentrations of the reagents. To confirm the validity of the kinetic mechanism proposed, we also performed a set of experiments at a different reaction temperature (45°C instead of 30°C). The values of the kinetic parameters so obtained are reported in *Table 2*.

Table 2 Kinetic parameters for Michael-type polyaddition reaction of monomer **I** towards **III** and **IV**

Vinyl ester	Temperature (°C)	k_2 (l^2 mol h^{-1})	k_3 (l^2 mol h^{-1})	k_3/k_2	k_2(**III**)/k_2	k_3(**III**)/k_3
III	30	0.5102	0.5423	1.06	1	1
IV	30	0.0146	0.0164	1.12	34.9	33.1
III	45	1.4400	1.3200	0.92	1	1
IV	45	0.0335	0.0300	0.85	43.0	44.0

A comparison between the numerical values of these parameters, at 30°C, gives a quantitative evaluation of the difference in reactivity between acrylic and methacrylic esters, which is already apparent by considering the kinetic curves obtained from the same experimental conditions (see *Figure 1*). This difference in reactivity also exists at 45°C, although the values of the ratios k_2(**III**)/k_2(**IV**) and k_3(**III**)/k_3(**IV**) at the two temperatures are fairly different, due to the different activation energy of the addition reaction for acrylates and methacrylates. The fact that kinetic equation (1) does not fit experimental data indicates that the reaction is catalysed by protogenic substances present in solution. Finally the ratio k_3/k_2 gives an indication of the relative contribution as proton-donor catalysts of **I** and tertbutyl alcohol. This ratio should be the same, the other conditions being equal, in both bisacrylates and methacrylate-based polyaddition. As clearly shown in *Table 2*, this is reasonably confirmed by our experimental data.

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