

Syntheses and Properties of Polymers from 1-Chloro-2,3-Epoxypropane and Amines

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Synopsis

1-Chloro-2,3-epoxypropane (CEP) reacts with excess of amines giving linear, thermally stable amino polymers, useful as dyeability modifiers for synthetic fibers. The polycondensation of 1-chloro-2,3-epoxypropane with amines is described, and preparations of such polymers are given: the polycondensations are carried out in one or two steps. In the first step, a mixture of polymeric aminochlorohydrins is formed. Alkalies added at the end of the polycondensations act as regulators of the molecular weight of the polymers obtained. The amino polymers, prepared with an excess of amines, have high melting temperatures, without decomposition; the weight losses in air at 250°C and 300°C are lower than those of the corresponding amino polymers prepared with deficient amounts of amines; the change of inherent viscosities due to thermal treatments is generally low.

INTRODUCTION

The reaction between 1-chloro-2,3-epoxypropane (CEP) and polyfunctional amines, employing an excess of CEP, gives crosslinked polymers, generally claimed as ion-exchange resins, which are insoluble in solvents and thermally unstable.

In Table I, some examples are shown of the syntheses and properties of some of these amino polymers, disclosed by the technical literature: the polymers melt at high temperatures, but with decomposition.¹⁻⁸ Another class of amino polymers was obtained by reaction of CEP and amines, with molar ratios CEP: amine lower than 1 (excess of amine); these polymers were claimed as dyeability modifiers for polypropylene fibers.^{9,10} Similar polymers were obtained by reacting amines with 2,3-epoxypropylamines.¹¹⁻¹⁴

The first class of amino polymers cannot be spun in blends with polypropylene, because of their low thermal stability; on the contrary, the second class is suitable to confer dyeability to polypropylene fibers, since the products of polycondensation are linear, thermally stable polymers, containing amino groups, and hydroxyls. If the modifiers contain tertiary amino groups, which can be converted into quaternary ammonium groups, their dyeability is remarkable, because tertiary amino and quaternary ammonium groups absorb dyes better than primary and secondary amino groups.¹⁵⁻¹⁸

Some information on the linear amino polymers from CEP and amines, and on their properties, were supplied in a previous communication.¹⁹ A description of the syntheses and properties of these polymers is given in this paper.

EXPERIMENTAL

Materials. 1-Chloro-2,3-epoxypropane (CEP), amines (*n*-dodecylamine, *n*-octadecylamine, ethylenediamine, diethylenetriamine, hexamethylenediamine,

TABLE I
 Synthesis and Properties of Crosslinked Polymers from 1-Chloro-2,3-Epoxypropane and Amines^a

Amines	Solvent	Synthesis			Properties		Ref.
		Time (h)	Temp (°C)	Molar ratio chloroepoxypropane/amines	N (%)	Melting (°C)	
Ethylendiamine	water	2.15	10-25	1:0.33	6.76	210 (dec.)	1
	methanol	—	40-60	1:0.50	9.70	72-76	2
Diethylenetriamine	water	2.15	10-25	1:0.40	10.90	213 (dec.)	1
	water	2.15	10-25	1:0.50	10.92	213 (dec.)	1
Dipropylenetriamine	water	0.50	50	1:0.33	10.30	213 (dec.)	3
	water	2.15	10-25	1:0.40	10.13	213 (dec.)	1
Tetraethylenepentamine	water	2.15	10-25	1:0.25	11.16	206 (dec.)	1
	water	2.15	10-25	1:0.28	11.80	235 (dec.)	1
	water	2.15	10-25	1:0.33	12.50	207 (dec.)	1
	water	0.50	50	1:0.33	7.20	—	3
	water	2.15	10-25	1:0.40	14.80	230 (dec.)	1
Aniline	methanol	3.00	65	1:0.46	6.80	—	4
2-Aminobenzoic acid	water	14.00	75-80	1:1.00	3.15	—	5
Piperazine	water	1.00	60	1:0.42	7.40	108	6
N,N'-Diaminopropylpiperazine	water	1.50	100	1:0.80	9.80	210 (dec.)	7
4,4'-Bipiperidine	ethanol/water	1.00	60	1:0.42	10.20	215 (dec.)	8

^a Specific viscosity and oxirane groups not measured because the polymers are insoluble in water and organic solvents.

dipropylenetriamine, tetraethylenepentamine, *N,N'*-dialkylhexamethylenediamines, aniline, piperazine, *N,N'*-diaminopropylpiperazine, 4,4'(bipiperidine), 2-aminobenzoic acid, 2,2-bis(4-hydroxyphenyl)propane, and 2,4-dimethyl-1,5-dichloromethylbenzene were purified by distillation or crystallization of commercial products. Poly(2-vinylpyridine) was obtained by polymerization of 2-vinylpyridine (supplied by Reilly Tar); the catalyst was 1-chlorobutane. Poly(hexamethyleneisocinchomeronamide) was obtained by melt polymerization of the salt from hexamethylenediamine and isocinchomeric acid (2,5-pyridinedicarboxylic acid).

Polycondensations. When only one amine was used, the solvent (generally alcohols), CEP, and the amine were placed in a 1000-mL flask, equipped with thermometer, stirrer, condenser, and dropping funnel. The solutions were heated at constant temperature for a definite time (generally 8 h), and then treated with alkalis and heated (8 h); the condensation polymers were isolated by removing the solvent under reduced pressure. In polycondensations of CEP with two or more amines, the solvent, CEP, and one amine—in a first step—were placed into a flask for a definite time; in a second step, solutions were added with CEP and the other amine, adjusting the total amounts of the reagents at a molar ratio of CEP to amines lower than 1.

Kinetics. The kinetics of reaction of CEP with *n*-octadecylamine, and of *N,N'*-bis(2,3-epoxypropyl)-*n*-octadecylamine with piperazine (Fig. 1) were followed by determination of oxirane groups (reaction with hydrochloric acid/dioxane) according to Ref. 20.

Characterization. The determination of amino + hydroxyl groups (Table II) was performed by acetylation (reaction with acetic anhydride/pyridine) ac-

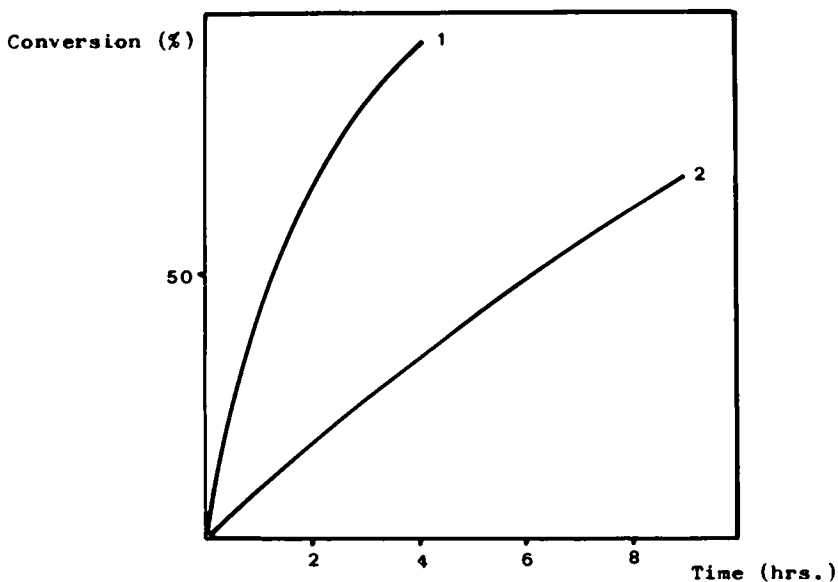


Fig. 1. Synthesis of poly(2-hydroxytrimethylene-co-piperazine-co-*n*-octadecylamine) in methanol at 65°C. (1) First step: reaction of 1-chloro-2,3-epoxypropane and *n*-octadecylamine. (2) Second step: reaction of *N,N'*-bis(2,3-epoxypropyl)-*n*-octadecylamine (formed in the first step) and piperazine.

TABLE II
 Products Obtained in Polycondensation of 1-Chloro-2,3-Epoxypropane and *n*-Octadecylamine in Methanol at 65°C

	Reaction products	Reaction time (h)	Mol weight	N _{tot} (%)	N ⁺ (%)	Cl _{tot} (%)	Cl ⁻ (%)	Amino + hydroxyl groups (%)
	Raw material, after drying (35°C/2 mm Hg)	3	690	3.30	1.50	14.40	4.00	7.00
	Products of fractional precipitation:	8	643	3.25	1.85	14.62	4.75	6.30
	1 fraction	8	900	3.50	1.60	9.10	4.50	6.00
	2 fraction	8	818	3.60	1.31	9.90	—	—
	3 fraction	8	750	3.45	1.74	9.81	4.44	6.80
	4 fraction	8	750	3.40	1.60	10.80	4.50	6.30
	5 fraction	8	745	3.50	1.60	10.70	4.70	6.40
	6 fraction	8	620	3.20	1.70	15.50	5.00	7.60
	Calculated values for		361.5	3.87	—	9.82	—	9.40
C ₂₁ H ₄₄ O ₂ NCl	CH ₂ Cl—CHOH—CH ₂ —NH—C ₁₈ H ₃₇							
C ₂ H ₄ O ₂ NCl ₂	CH ₂ Cl—CHOH—CH ₂ —N—CH ₂ CHOH—CH ₂ Cl C ₁₈ H ₃₇		454.0	3.08	—	15.64	—	7.09
C ₄ H ₈ O ₂ N ₂ Cl ₂	CH ₂ Cl—CHOH—CH ₂ —N—CH ₂ CHOH—CH ₂ NH—C ₁₈ H ₃₇ Cl ⁻ H ⁺		723.0	3.87	1.93	9.82	4.91	7.05
C ₄ H ₈ O ₃ N ₂ Cl ₃	CH ₂ Cl—CHOH—CH ₂ —N—CH ₂ CHOH—CH ₂ —N—CH ₂ CHOH—CH ₂ Cl Cl ⁻ H ⁺ C ₁₈ H ₃₇		815.5	3.43	1.71	13.06	4.35	6.25

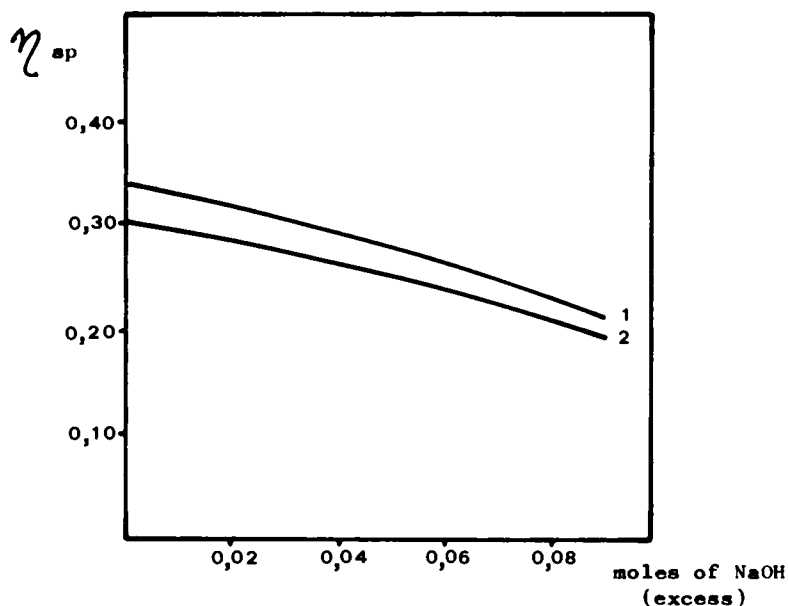


Fig. 2. Control of molecular weight by excess of NaOH (with respect to amount necessary for complete neutralization) in polycondensation of 1-chloro-2,3-epoxypropane (1 mol) with *n*-octadecylamine (0.235 mol) and piperazine (0.77 mol). Solvents: (1) ethanol; (2) methanol.

according to Ref. 21. The fractional precipitation (Table II) was performed by filtration of polymers spontaneously precipitated. The inherent and specific viscosities were measured at 25°C with a Desreux-Bischoff viscosimeter in solutions in isopropyl alcohol (concentrations: 0.5%, inherent viscosity; 1%, specific viscosity). The molecular weights of polymers were determined according to the ebullioscopic method, with a Ray modified ebulliometer.²² The thermal stability was determined by measuring the viscosities of polymers before and after thermal treatment (260°C/6 h, in nitrogen) and by measuring the weight losses at 250°C and 300°C in air with a Perkin-Elmer TGS-1 Thermobalance (heating rate = 4°C/min).

RESULTS AND DISCUSSION

Syntheses and Kinetics

CEP can react with one or more amines, with molar ratios lower than 1 (excess of amine), to give linear, thermally stable amino polymers. The reaction with only one amine occurs easily, and its kinetics depend on the reactivity of the amine. Using more than one amine, it is necessary to consider the different reactivity of amines, in order to avoid the formation of blends of two or more polymers with different compositions.

The polycondensation of CEP with two amines must be carried out in two steps: in the first one, an excess of CEP is reacted with one amine; in the second one, the reaction products are reacted with the other amine and with another amount of CEP, so as to adjust the total amounts of the reagents to molar ratios lower than one.

TABLE III
Melting Temperatures of Polymers from 1-Chloro-2,3-Epoxypropane and Amines

Polymers	Molar ratio chloroepoxy propane:amines	Melting temperatures (°C)
Poly(2-hydroxytrimethylene-co-piperazine)	1:1	202-208
Poly(2-hydroxytrimethylene-co- <i>N,N'</i> -bis(2,2,6,6-tetramethylpiperidine)hexamethylenediamine)	1:1	54-58
Poly(2-hydroxytrimethylene-co- <i>n</i> -dodecylamine-co-hexamethylenediamine)	1:0.5:0.6	120
Poly(2-hydroxytrimethylene-co- <i>n</i> -octadecylamine-co-hexamethylenediamine)	1:0.5:0.6	105-110
Poly(2-hydroxytrimethylene-co-piperazine-co- <i>n</i> -octadecylamine)	1.3:1:0.3 ₁	55-58
Poly(2-hydroxytrimethylene-co-piperazine-co-2,2-bis(4-hydroxyphenyl)propane)	1.2:1:0.2 ₁	130-140
Poly(2-hydroxytrimethylene-co-piperazine-co- <i>N,N'</i> -dicyclohexylhexamethylenediamine)	1.2:1:0.2 ₁	150-170
Poly(2-hydroxytrimethylene-co-piperazine-co- <i>N,N'</i> -dicyclohexylhexamethylenediamine)	1.3:1:0.3 ₁	155-170
Poly(2-hydroxytrimethylene-co-piperazine-co-2,4-dimethyl-1,5-dimethylenebenzene)	0.6:1:0.4 ₁	190-204

In the first step, chlorohydrins of amines are formed, which can give epoxy derivatives in the presence of basic catalysts (amines).²³ These epoxy compounds, together with the chlorohydrins of amines and the remaining amount of CEP, react in the second step with the other amine.

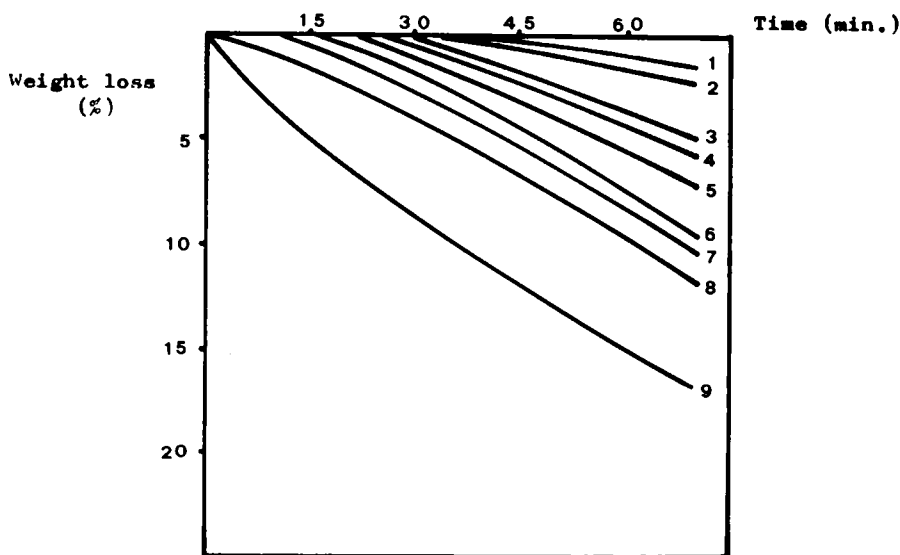


Fig. 3. Thermal stability of some amino polymers in air at 250°C: (1) poly(2-hydroxytrimethylene-co-*N,N'*-bis(2,2,6,6-tetramethylpiperidine)-hexamethylenediamine); (2) poly(2-hydroxytrimethylene-co-piperazine-co-*N,N'*-bis(cyclohexyl)-hexamethylenediamine); (3) poly(2-hydroxytrimethylene-co-piperazine-co-2,4-dimethyl-1,5-dimethylenebenzene); (4) poly(2-hydroxytrimethylene-co-piperazine-co-*n*-dodecylamine); (5) poly(2-hydroxytrimethylene-co-piperazine-co-2,2-bis(4-hydroxyphenyl)propane); (6) poly(2-hydroxytrimethylene-co-piperazine); (7) poly(hexamethyleneisocinchomeramide); (8) poly(2-vinylpyridine).

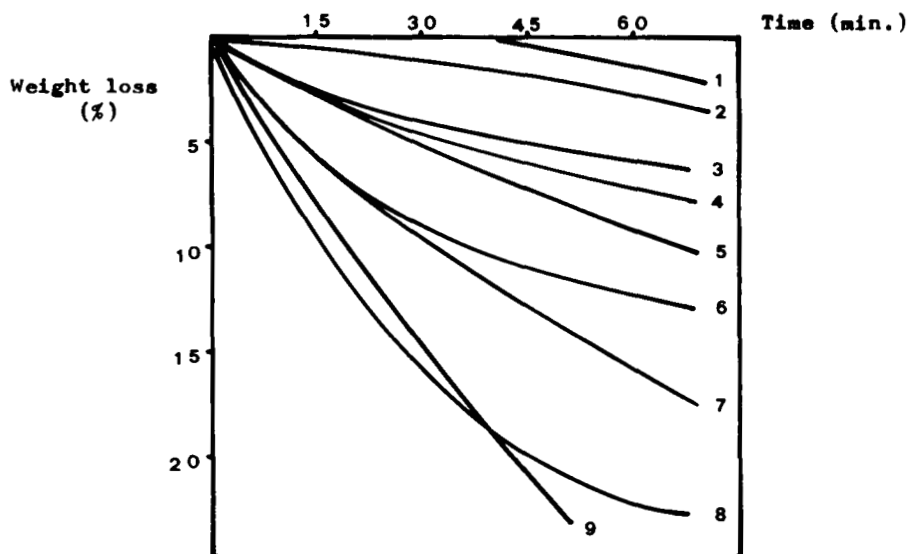


Fig. 4. Thermal stability of some amino polymers in air at 300°C. (1) poly(2-hydroxytrimethylene-co-*N,N'*-bis(2,2,6,6-tetramethylpiperidine)hexamethylenediamine); (2) poly(2-hydroxytrimethylene-co-piperazine-co-*N,N'*-bis(cyclohexyl)hexamethylenediamine); (3) poly(2-hydroxytrimethylene-co-piperazine-co-2,4-dimethyl-1,5-dimethylenebenzene); (4) poly(2-hydroxytrimethylene-co-piperazine-co-2,2-bis(4-hydroxyphenyl)propane); (5) poly(2-hydroxytrimethylene-co-piperazine); (6) poly(2-hydroxytrimethylene-co-piperazine-co-*n*-dodecylamine); (7) poly(2-hydroxytrimethylene-co-piperazine-co-*n*-octadecylamine); (8) poly(hexamethyleneisochinonamide); (9) poly(2-vinylpyridine).

As an example, the kinetics of the preparation in two steps of poly(2-hydroxytrimethylene-co-piperazine-co-*n*-octadecylamine) is represented in Figure 1. In the first step (curve 1) the amine with lower reactivity (*n*-octadecylamine)

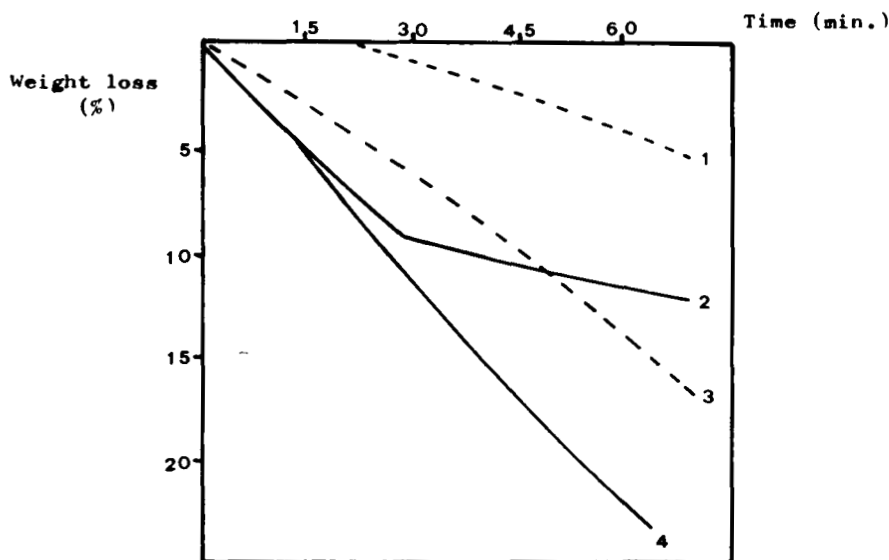


Fig. 5. Thermal stability of poly(2-hydroxytrimethylene-co-*n*-dodecylamine-co-piperazine) (1, 2) and poly(2-hydroxytrimethylene-co-*n*-dodecylamine-co-hexamethylenediamine) (3, 4) in air at 250°C (---, 1, 3), and at 300°C (—, 2, 4).

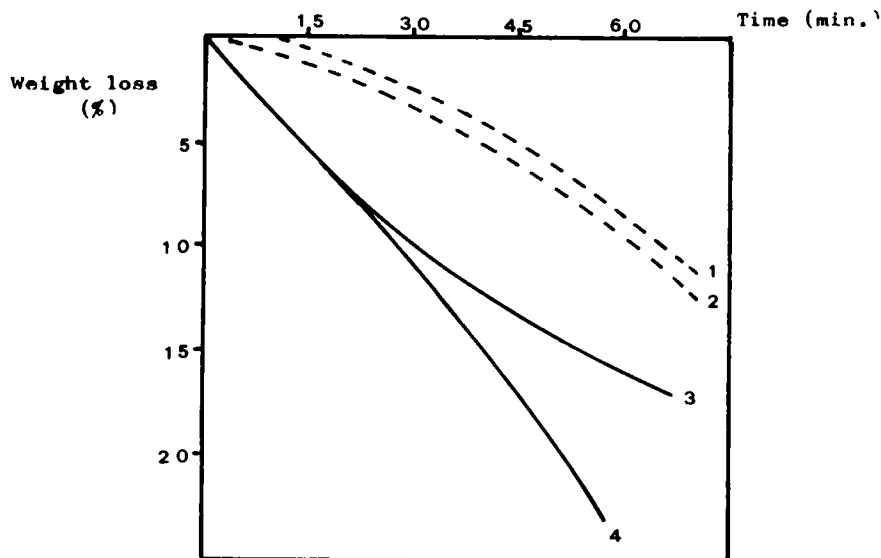


Fig. 6. Thermal stability of poly(2-hydroxytrimethylene-co-*n*-octadecylamine-co-piperazine) (1, 3) and poly(2-hydroxytrimethylene-co-*n*-octadecylamine-co-hexamethylenediamine) (2, 4) in air at 250°C (---, 1, 2), and at 300°C (3, 4).

and in the second step the amine with higher reactivity (piperazine) take part in reaction: in such conditions it is possible to obtain a copolymer CEP/*n*-octadecylamine/piperazine; on the contrary in the simultaneous reaction of CEP and the same amines copolymers CEP/*n*-octadecylamine and CEP/piperazine are obtained.

The products obtained in the first step of this polycondensation have the structures and compositions shown in Table II: molecular weights and analytical data point out that in the first step of the reaction CEP and *n*-octadecylamine form a mixture of polymeric amino chlorohydrins. At the end of the polycondensations, the polymers are treated with alkalis, which act not only to neutralize the hydrochloric acid bound to the amino groups but also act regulating the molecular weight of polymers, when used in excess of the amount required for the complete neutralization, as shown in Figure 2.

Properties of Amino Polymers

The comparison of the melting temperatures of some amino polymers obtained with deficient (Table I) and excess amounts (Table III) of amines shows that the melting temperatures are generally high, without decomposition, when the polymers are prepared in excess of amine. The thermal stability of the amino polymers is demonstrated by weight loss measurements at different temperatures and by changes in inherent viscosities after thermal treatments.

Weight losses of amino polymers from CEP at 250°C and 300°C in air, represented in Figures 3 and 4, are lower than those of other amino polymers claimed as dyeability modifiers. The higher stability is due to polymers containing piperidine, piperazine, cyclohexane, and aromatic rings, while aliphatic structures present lower stability, which is better, however, than that of polymers from CEP and amines that have been prepared with deficient amounts of amine (Table I).

TABLE IV
Effect of Chemical Structure and Composition on Thermal Stability of Polymers

Polymers	Molar ratio chloroepoxy propane:amines	Inherent viscosity	
		Starting	After 6 h at 260°C in nitrogen
Poly(2-hydroxytrimethylene-co-piperazine)	1:1	0.45	0.42
	1:1	0.36	0.33
	1:1	0.33	0.29
Poly(2-hydroxytrimethylene-co- <i>N,N'</i> -bis(2,2,6,6-tetra- methylpiperidine)hexamethylenediamine)	1:1	0.10	0.10
	1:1	0.09	0.09
	1:1	0.08	0.08
Poly(2-hydroxytrimethylene-co-piperazine-co- <i>n</i> -dodec- ylamine)	1.2:1:0.2 ₁	0.34	0.25
	1.3:1:0.3 ₁	0.27	0.22
	1.5:1:0.5 ₁	0.21	0.17
Poly(2-hydroxytrimethylene-co-piperazine-co- <i>n</i> -octade- cylamine)	1.3:1:0.3 ₁	0.31	0.30
	1.3:1:0.3 ₁	0.19	0.19
	1.3:1:0.3 ₁	0.18	0.17
Poly(2-hydroxytrimethylene-co-piperazine-co-2,4-dime- thyl-1,5-dimethylenebenzene)	0.5:1:0.5 ₁	0.27	0.25
	0.6:1:0.4 ₁	0.36	0.32
	0.7:1:0.3 ₂	0.43	0.35

TABLE V
Effect of Alkyls on Thermal Stability of Poly(2-hydroxytrimethylene-co-Piperazine-co-*N,N'*-
dialkylhexamethylenediamine):

R	Molar ratio chloro- epoxypropane:pipera- zine:dialkylhexa- methylenediamine	Inherent viscosity	
		Starting	After 6 h at 260°C in nitrogen
—CH ₂ CH—CH ₂ — OH	1.5:1:0.5 ₁	0.20	0.20
	1.3:1:0.3 ₁	0.28	0.25
	1.2:1:0.2 ₁	0.33	0.30
—CH—CH ₃ CH ₃	1.3:1:0.3 ₁	0.18	0.17
	1.2:1:0.2 ₁	0.19	0.19
—CH ₂ —CH ₂ —CH ₂ —CH ₃	1.3:1:0.3 ₂	0.21	0.21
	1.2:1:0.2 ₁	0.25	0.23
—CH ₂ CH—CH ₃ CH ₃	1.3:1:0.3 ₄	0.20	0.20
	1.3:1:0.3 ₁	0.18	0.17
—CH—CH ₂ —CH—CH ₃ CH ₃	1.3:1:0.3 ₁	0.33	0.32
	1.5:1:0.5 ₁	0.25	0.23
—CH ₂ —(CH ₂) ₆ —CH ₃	1.3:1:0.3 ₁	0.31	0.27
	1.2:1:0.2 ₁	0.36	0.35

Polymers from CEP and amines containing primary amino groups present higher weight losses than polymers from CEP and amines containing secondary amino groups: in Figures 5 and 6, the behavior is compared with polymers containing structural units of piperazine (two secondary amino groups) and

hexamethylenediamine (two primary amino groups). Moreover, the size of the aliphatic units affects the thermal stability of these polymers: the smaller the aliphatic units, the higher the stability (Figs. 3 and 4).

The change of inherent viscosity due to thermal treatments is very low in polymers from CEP prepared in excess of amine (Table IV). The effect of size of alkyl groups is represented in Table V: the inherent viscosities of polymers containing alkyls from C₁ to C₈, and the cyclohexyl group are not affected by thermal treatments; the molar ratios of components are also not influential.

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