

Synthesis and Characterization of Poly(ester–amide)s from Bis(2-oxazoline)s, Anhydrides, and Diols

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ABSTRACT: A new class of poly(ester–amide)s was prepared by reacting bis(2-oxazoline)s, carboxylic anhydrides, and diols of different structures. The polymerization proceeds through the formation of a dicarboxy ester by reaction of two anhydride molecules with one diol molecule and subsequent 2-oxazoline ring opening by attack of the dicarboxy ester. The whole process leads to linear poly(ester–amide)s, whose structures were established by carbon and proton NMR analysis. The thermal characteristics of the prepared polymers were studied by differential scanning calorimetry. Transition temperatures were found to increase with an increase in the polymer chain stiffness. Poly(ether–ester–amide)s were also prepared by employing poly(ethylene glycol) as a comonomer, alone, or in a mixture with ethylene glycol, thus obtaining block segmented polymers.

Introduction

Cyclic bis(imino ether)s, namely, bis(2-oxazoline)s or bis(5,6-dihydro-4*H*-1,3-oxazine)s, are versatile bifunctional compounds reactive toward molecules containing several kinds of reactive groups.^{1–3}

Several works describe the use of monofunctional 2-oxazolines as monomers for the synthesis of poly(*N*-acylimine)s through cationic polymerization.^{4–7} Copolymerization with electrophilic comonomers such as β -methylhydrogen itaconate,⁸ tetrachlorophthalic anhydride,⁹ succinic anhydride,^{10,11} phthalic anhydride,^{12,13} or acrylic acid¹⁴ proceeds via zwitterion intermediates. Step-growth polymerization of bis(2-oxazoline)s with acidic comonomers such as carboxylic diacids,^{15–19} thio-carboxylic acids,²⁰ dithiols,²¹ and diphenols²² leads to linear polymers containing amide groups. Moreover, polymerizations of monomers containing one imino ether ring and another functional group (for instance, carboxylic, phenolic, or thiolic) are reported.^{23,24}

The reaction of bis(2-oxazoline)s with diacids according to Scheme 1 (R, R' = divalent radicals) results in a step-growth polyaddition mechanism and gives linear poly(ester–amide)s.^{15–19}

In principle, the diacid could be a dicarboxy ester prepared *in situ* by reacting a diol with a monoanhydride, according to Scheme 2 (A, D = divalent radicals).

However, since anhydrides themselves are reactive toward 2-oxazolines^{9–13} (Scheme 3a; A = divalent radicals; Q = monovalent radical), if bifunctional oxazolines are reacted with monoanhydrides, a cross-linked infusible polymer would be obtained (a polymer containing ester, imide, imine, and anhydride groups), according to Scheme 3b (A, R = divalent radicals).

A cross-linked polymer [poly(*N*-acylimine)] would also be formed due to the possible cationic homopolymerization of bis(2-oxazoline)s initiated by acid compounds⁶ (Scheme 4; R = divalent radical).

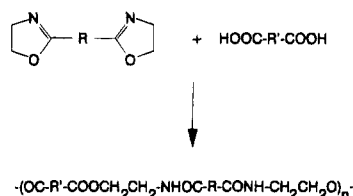
All the described mechanisms are competitive in the polymerization of bis(2-oxazoline)s with anhydrides and diols, and thus it is not straightforward to foresee the structure and the properties of the polymers obtained through this reaction.

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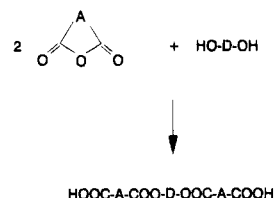
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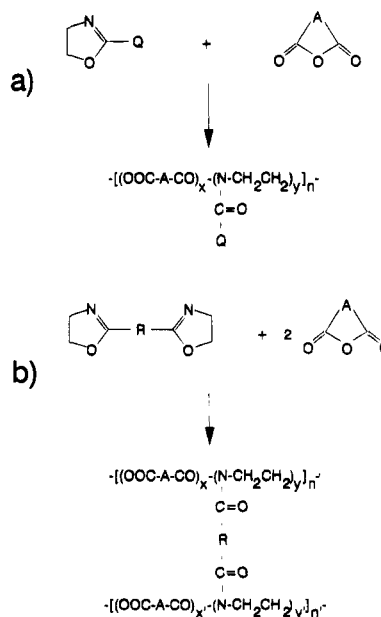
Scheme 1



Scheme 2



Scheme 3



The aim of the present work is to report on the synthesis of poly(ester–amide)s prepared from bis(2-oxazoline)s, monoanhydrides, and several different diols as starting monomers and to elucidate their chemical structure.

Scheme 4

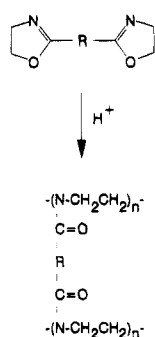
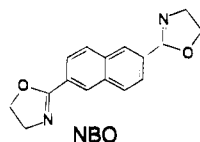
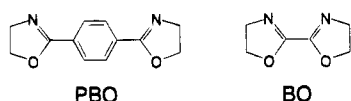
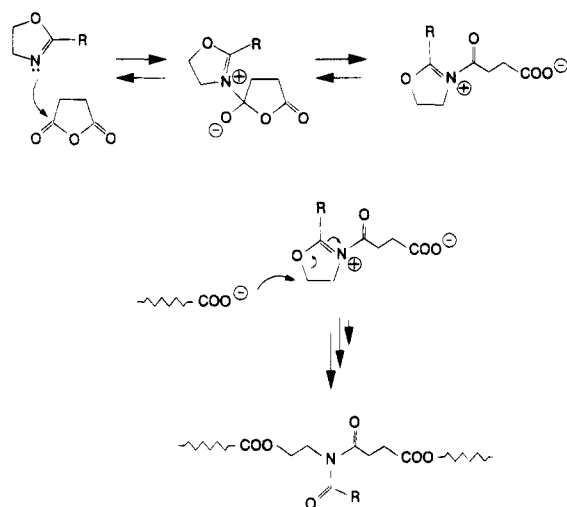


Chart 1



Scheme 5



Results and Discussion

Two different bis(2-oxazoline)s were mainly considered in this study: 2,2'-(1,4-phenylene)bis(2-oxazoline) (PBO) and 2,2'-bis(2-oxazoline) (BO). 2,2'-(2,6-Naphthylene)bis(2-oxazoline) (NBO) was used in one further polymerization. Their chemical structures are reported in Chart 1.

Preliminary studies were accomplished to establish the reactivity of 2-oxazolines with either alcohols or anhydrides. 2-Oxazolines are inert toward aliphatic diols: after treating PBO with ethylene glycol at 190 °C for 90 min, the starting unreacted products were recovered. By treating PBO with succinic anhydride, in the absence of other comonomers, the mixture solidifies abruptly within 2–3 min from the beginning of the reaction. A product was recovered, insoluble in all common organic solvents, which decomposes without melting during DSC analysis. This event is an obvious indication that a cross-linked resin has been obtained, according to Scheme 3b (the reaction mechanism is reported in Scheme 5).

Table 1. Characteristics of Poly(ester–amide)s from 2,2'-(1,4-Phenylene)bis(2-oxazoline) and Succinic Anhydride

sample	diol	reaction temp (°C)	IV ^a (dL/g)	T _g (°C)	T _m (°C)	H _m (J/g)
EG/S/PBO	ethylene glycol	200	0.24	32		
DEG/S/PBO	diethylene glycol	170	0.38	16		
TEG/S/PBO	triethylene glycol	140	0.43	6		
PD/S/PBO	1,3-propanediol	190	0.40	22		
PG/S/PBO	1,2-propanediol	200	0.47	34		
NPG/S/PBO	neopentyl glycol	180	0.31	30		
BD/S/PBO	1,4-butanediol	180	0.47	21	155	9.5
HD/S/PBO	1,6-hexanediol	170	0.48	23	142	2.1
DD/S/PBO	1,12-dodecanediol	160	0.40	13	149	34
CHD/S/PBO	1,4-cyclohexanediol	200	0.42	52		
CHM/S/PBO	1,4-cyclohexanedimethanol	190	0.33	45		
BDM/S/PBO	1,4-benzenedimethanol	220	0.30	52	172	
BHP/S/PBO	N,N'-bis(2-hydroxyethyl)piperazine	200	0.15	39	169	5.1

^a Inherent viscosity.

Table 2. Characteristics of Poly(ester–amide)s from 2,2'-Bis(2-oxazoline) and Succinic Anhydride

sample	diol	reaction temp (°C)	IV ^a (dL/g)	T _g (°C)	T _m (°C)	H _m (J/g)
EG/S/BO	ethylene glycol	150	0.13	5		
DEG/S/BO	diethylene glycol	140	0.13	3		
TEG/S/BO	triethylene glycol	130	0.12	–13		
PD/S/BO	1,3-propanediol	150	0.13	7		
PG/S/BO	1,2-propanediol	160	0.12	11		
NPG/S/BO	neopentyl glycol	160	0.23	18		
BD/S/BO	1,4-butanediol	130	0.13	–2	105	1.0
HD/S/BO	1,6-hexanediol	150	0.29	3	110	28
DD/S/BO	1,12-dodecanediol	140	0.14	0	121	51
CHD/S/BO	1,4-cyclohexanediol	170	0.13	33		
CHM/S/BO	1,4-cyclohexanedimethanol	160	0.17	22		
BDM/S/BO	1,4-benzenedimethanol	160	0.14	25		
BHT/S/BO	bis(2-hydroxyethyl)-terephthalate	170	0.12	28		
BHP/S/BO	N,N'-bis(2-hydroxyethyl)piperazine	160	0.13	21	133	4.3

^a Inherent viscosity.

In Table 1 polymers prepared from succinic anhydride (S), BO, and diols are reported; properties of polymers from succinic anhydride, PBO, and diols are reported in Table 2, while Table 3 summarizes the characteristics of polymers from phthalic anhydride (F), PBO, and diols. Finally, one polymer was prepared from succinic anhydride, NBO, and 1,6-hexanediol.

The polymers were prepared in a one-pot synthesis by mixing the bis(2-oxazoline), the anhydride, and the diol in the molar ratio 1:2:1 without any solvent (attempts to perform the polymerization in chlorobenzene or *N*-methylpyrrolidone failed) and heating the mixture at temperatures between 130 and 210 °C. Higher reaction temperatures were required by lower molecular weight diols or the stiffer bis(2-oxazoline)s (NBO > PBO > BO) or anhydrides (phthalic > succinic) to maintain the reaction mixture in the molten state.

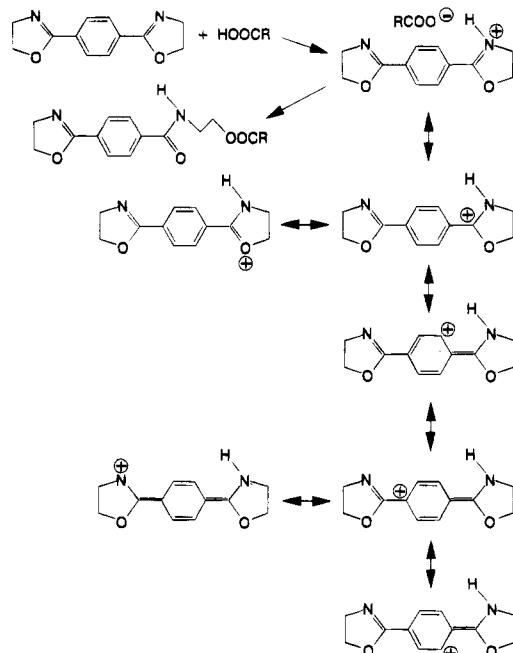
The described polymerization runs were performed without catalyst, although quaternary ammonium salts,²⁵ quaternary phosphonium salts, and tertiary phosphines²⁶ are reported to catalyze the reaction of bis(2-oxazoline)s with carboxylic groups.

The reaction time was fixed at 90 min, but by reducing reaction times up to 20 min, polymers with almost unchanged properties were obtained.

In general, most poly(ester–amide)s from BO were dark brown in color; polymers from PBO and NBO had

Table 3. Characteristics of Poly(ester-amide)s from 2,2'-(1,4-Phenylene)bis(2-oxazoline) and Phthalic Anhydride

sample	diol	reaction temp (°C)	IV ^a (dL/g)	T _g (°C)
EG/F/PBO	ethylene glycol	200	0.12	66
DEG/F/PBO	diethylene glycol	160	0.12	59
TEG/F/PBO	triethylene glycol	150	0.17	40
PD/F/PBO	1,3-propanediol	190	0.16	58
PG/F/PBO	1,2-propanediol	190	<0.1	79
NPG/F/PBO	neopentyl glycol	180	0.15	72
BD/F/PBO	1,4-butanediol	180	0.14	50
HD/F/PBO	1,6-hexanediol	170	0.20	40
OD/F/PBO	1,8-octanediol	160	<0.1	26
ND/F/PBO	1,9-nonanediol	160	<0.1	27
TD/F/PBO	1,10-decanediol	160	<0.1	25
DD/F/PBO	1,12-dodecanediol	160	0.21	20

^a Inherent viscosity.**Scheme 6**

amber to brown colors, with darker tones for the samples synthesized at higher temperatures. The color usually set up very quickly after monomer melting and was accompanied by a sudden increase in melt viscosity. The development of violet–purple colors was observed during the polymerizations from PBO and NBO, possibly associated with the formation of heterocyclic reaction intermediates bearing delocalized charges (Scheme 6). Afterward the violet often faded to amber or gray.

Strong indications that the polymer structure is not cross-linked are (a) attainment of viscous polymer melts, (b) polymer solubility in dimethylformamide, dimethylacetamide, *N*-methylpyrrolidone, dimethyl sulfoxide, and *m*-cresol, and (c) thermal properties (see below).

Nonetheless, these facts do not exclude that the reactions outlined in Schemes 3 and 4 could proceed in some extent, causing a partial branching. Indeed as described at the beginning of the paragraph, by reacting PBO with succinic anhydride a cross-linked polymer is quickly obtained. Thus, nuclear magnetic resonance studies were accomplished to elucidate the polymer structure.

Nuclear Magnetic Resonance Characterization.

To establish whether the structure of poly(ester-

Table 4. ¹³C-NMR Chemical Shift of EG/S/PBO, DD/S/PBO, and PG/S/PBO in DMSO-*d*₆ at 313 K

residue ^a	C _n ^a	chemical shift		
		EG/S/PBO	DD/S/PBO	PG/S/PBO
Ox	1	38.3	38.3	38.3
	2	62.5	62.5	62.5
T	1	136.6	136.5	136.5
	2	127.1	127.1	127.9
	3	165.9	165.8	165.8
S	1,1'	28.6	28.6	28.7–28.5
	2,2'	28.5	28.5	28.4
	3,3'	171.8	171.8	171.6–171.8
	4,4' ^b	171.9	171.8	171.3
EG	1	62.0		
DD	1		63.9	
PG	1			68.0
	2			15.9
	3			65.4

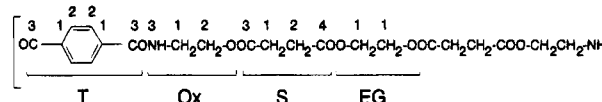
^a Residues and carbons (C_n) labeled according to Chart 2.^b Assignments can be interchanged.**Table 5. ¹H-NMR Chemical Shift of EG/S/PBO, DD/S/PBO, and PG/S/PBO in DMSO-*d*₆ at 353 K**

residue ^a	H _n ^a	chemical shift ^b		
		EG/S/PBO	DD/S/PBO	PG/S/PBO
Ox	3	8.38 (t)	8.37 (t)	8.68 (t)
	1	3.61 (q)	3.61 (q)	3.58 (q)
	2	4.3–4.2	4.27 (t)	4.22 (t)
T	2	7.97 (s)	7.97 (s)	7.96 (s)
S	1,1', 2,2'	2.64 (s)	2.64 (s)	2.61 (s)
EG	1	4.3–4.2		
DD	1		4.80 (t)	
PG	1			5.05 (sex)
	2			1.19 (m)
	3			4.11 (d)

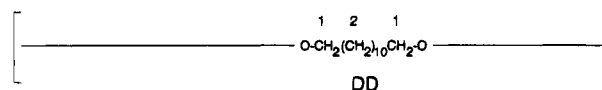
^a Residues and protons (H_n) labeled according to Chart 2. ^b s = singlet, d = doublet, t = triplet, q = quartet, sex = sextet, m = multiplet.

Chart 2

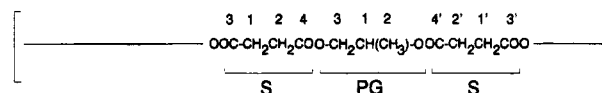
EG/S/PBO



DD/S/PBO



PG/S/PBO



amide)s is linear or possibly branched in part, samples were characterized by ¹H- and ¹³C-NMR analysis. Only EG/S/PBO, PG/S/PBO, and DD/S/PBO (EG = ethylene glycol, PG = 1,2-propanediol, DD = 1,12-dodecanediol) were considered in the following discussion, since they represent three typical situations. Carbon and proton chemical shifts are reported in Tables 4 and 5, respectively, while nuclei labeling is reported in Chart 2.

The ¹H-NMR spectrum of the sample DD/S/PBO is reported in Figure 1. The triplet at 8.4 ppm and the quartet at 3.6 ppm turned singlet and triplet, respectively, after addition of CF₃COOD and therefore are assigned to amidic (Ox₃) and Ox₁ protons, respectively. The signal at 4.3 ppm arises from DD₁, while that at

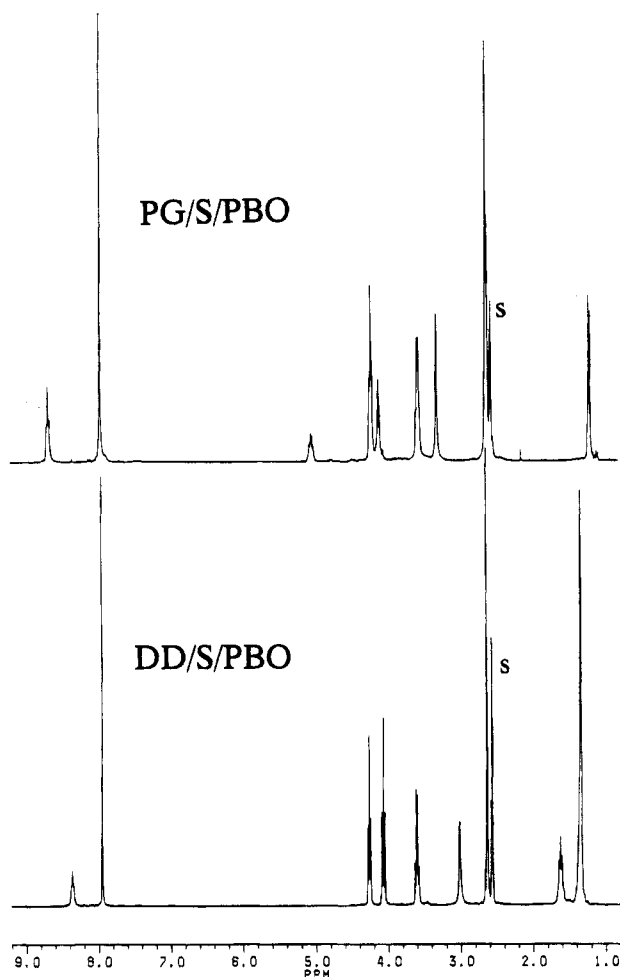


Figure 1. ^1H -NMR spectra of DD/S/PBO (bottom) and PG/S/PBO (top) in $\text{DMSO}-d_6$ at 353 K (S = solvent).

2.6 ppm arises from both methylene groups of the succinoyl residue. Aside from the most intense peaks, small resonances appear (<5%) which likely arise from end groups. In particular, the small quartet at 3.5 ppm (about 3.5% of the main quartet) became a triplet after treatment with CF_3COOD and is assigned to a terminal $-\text{CONHCH}_2-$ group. In any case the quartet sum corresponds stoichiometrically to the aromatic proton intensity, thus ruling out the occurrence of branching which is supposed to yield $-\text{CON}(\text{CH}_2)_2-$ fragments. The intensities of the main and of the terminal groups give a diol/anhydride/bis(2-oxazoline) molar ratio of 1:1.9:1, very close to the predicted value.

The ^{13}C -NMR spectrum reported in Figure 2 substantially confirms the considerations made on the basis of the proton spectrum and shows the presence of some peaks of very low intensity structurally related to the main peaks, very likely due to end groups.

Therefore, from these data we suggest that the polymerization proceeds according to the mechanism reported in Scheme 7.

The mechanism of Scheme 7, which results from a combination of reactions of Schemes 1 and 2, does not involve a direct reaction between the bis(2-oxazoline) and the anhydride.

Also for the sample PG/S/PBO it is possible to assert that the macromolecular chain is unbranched. Again the monomer ratio as derived from the signal intensity is in agreement with the theoretical one. Interestingly, as compared with the previous sample the ^{13}C -NMR signal (Figure 2) of the succinoyl moiety exhibits a

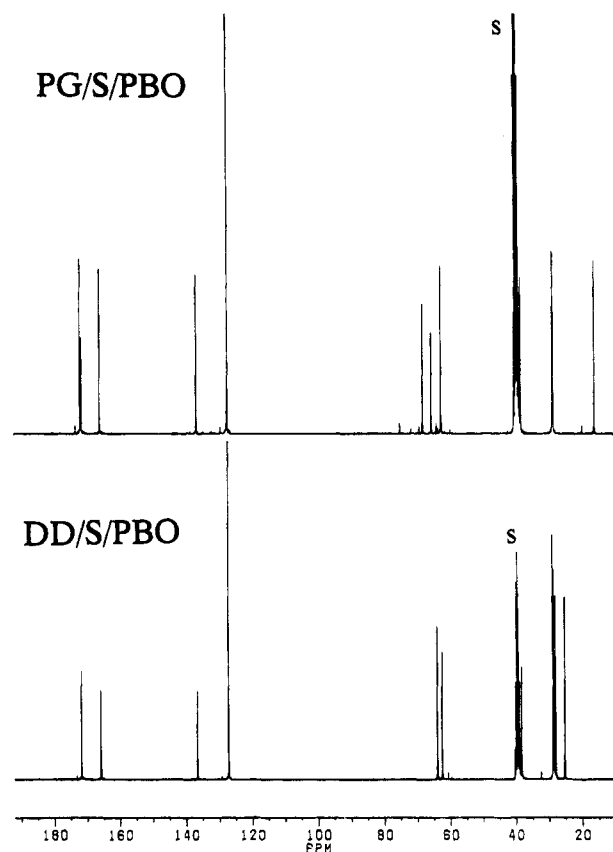
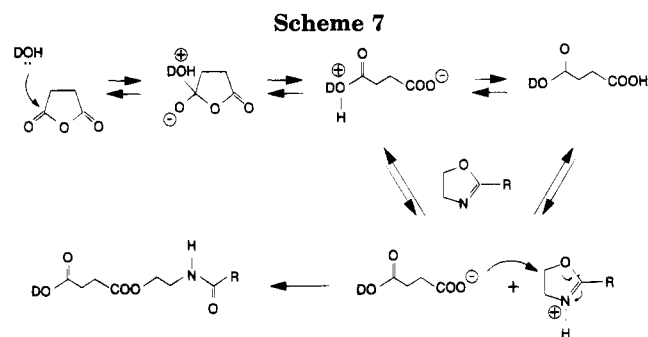


Figure 2. ^{13}C -NMR spectra of DD/S/PBO (bottom) and PG/S/PBO (top) in $\text{DMSO}-d_6$ at 313 K (S = solvent).



multiplicity arising from the asymmetry of 1,2-propylidene units. In fact, the $\text{C}=\text{O}$ region shows three peaks at 171.8, 171.6, and 171.3 ppm in a ratio 2:1:1, and the methylene protons show three resonances at 28.8, 28.5, and 28.4 ppm in a ratio 1:2:1. Considering a fragment centered on a 1,2-propylidene unit, succinoyl residues have two equivalent carbonyl groups (S_3 and S_3') bonded to the 2-oxazoline residue and two nonequivalent carbonyl groups (S_4 and S_4') bonded to either side of the 1,2-propylidene unit. The same arguments apply to S_1 , S_2 , S_1' , and S_2' methylene protons (see the ^1H -NMR spectrum, Figure 1).

The amidic and the Ox_1 protons of EG/S/PBO show a triplet at 8.4 ppm and a quartet at 3.6 ppm, respectively; the peaks corresponding to EG_1 protons appear at 4.3–4.2 ppm together with 2-oxazoline methylene groups bonded to succinoyl units. The succinoyl residue signal occurs at 2.6 ppm. Also in this sample small resonances (<5%) due to end groups are found. In particular, the quartet arising from $-\text{CONHCH}_2-$ end groups (2% of the main quartet) is found at 3.4 ppm. The sum of both quartets corresponds stoichiometrically to the aromatic proton intensity, thus excluding the presence of branch-

ing. Furthermore, a triplet appears at 4.1 ppm (about 3% of the multiplet at 4.3–4.2 ppm) which has a hidden counterpart at 3.6 ppm, i.e., under the Ox_2 pattern. This triplet is likely due to terminal hydroxyethylenic units. The monomer ratio 2-oxazoline/anhydride/diol calculated from the intensities of the main peaks and including the above-identified end groups is 1:1.8:1.

The observed slight discrepancies between experimentally determined monomer ratios and the theoretical ones for PG/S/PBO and EG/S/PBO samples could arise from the severe polymerization conditions. The polymerizations were performed at 200 °C (in the case of DD/S/PBO the reaction temperature was only 150 °C). It is very reasonable to admit that some succinic anhydride can sublime before it polymerizes. Indeed the formation of some small needles on the stirrer shaft was observed during this polymerization and during other polymerizations performed at high temperatures.

Thermal Characterization. The thermal transition temperatures of the various samples are reported in Tables 1–3. Sample HD/S/NBO (HD = 1,6-hexanediol) has a T_g of 33 °C and has no melting temperature. As a general characteristic, most poly(ester-amide)s are amorphous. Some samples exhibit multiple exo- and endotherms in the first heating scan, which disappear in the second heating scan: only a few polymers retain a melting peak in the second scan. In the tables the temperatures corresponding to these peaks are reported.

In particular, all the samples from phthalic anhydride (Table 3) are amorphous; among the polymers belonging to S/PBO and S/BO series (Tables 1 and 2, respectively) based on α,ω -diols $HO(CH_2)_nOH$, only those with $n \geq 4$ have a melting endotherm. The other polymers showing melting endotherms are those from N,N' -bis(2-hydroxyethyl)piperazine (BHP), which melted at 133 °C (BHP/S/BO) and 169 °C (BHP/S/PBO), and BDM/S/PBO (T_m = 172 °C; BDM = 1,4-benzenedimethanol). With rare exceptions, melting enthalpies are rather low.

DD/S/BO is the only polymer able to crystallize during cooling from the melt at the chosen scanning rate (10 °C/min). In all the other cases the crystallization occurs during the subsequent heating. Accordingly, an exothermic peak preceded the endothermic melting peak during the second scan.

These data suggest that the presence of cyclic residues and the absence of long alkylene chains reduce the polymer mobility in the melt, making it difficult to achieve ordered, crystalline structures.

Glass transition temperature (T_g) values are strictly related to the polymer structure. Intermolecular hydrogen bonding very likely plays a similar role in all the samples; thus, T_g behavior can be interpreted on the basis of the stiffness of the macromolecular segments.²⁷

For a given diol, the increase of 2-oxazoline stiffness leads to an increase in the glass transition temperature; for instance, the glass transition temperatures in the set HD/S/BO–HD/S/PBO–HD/S/NBO are 3, 23, and 33 °C, respectively. Substitution of succinic anhydride with phthalic anhydride causes an increase of T_g of about 20–40 °C, as shown from the comparison of S/PBO and F/PBO series (Tables 2 and 3): the phenylene ring of the phthaloyl residue reduces the chain flexibility with respect to the ethylene moiety of the succinoyl group.

Poly(ester-amide)s obtained varying the diol structure show glass transition temperatures which increase with an increase in diol stiffness. Polymers of diols

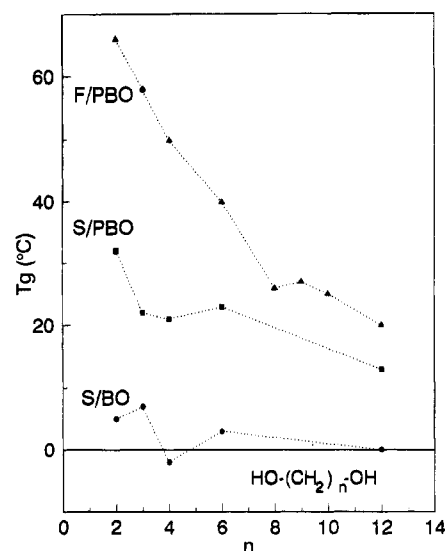


Figure 3. Glass transition temperatures of several series of poly(ester-amide)s as a function of the number of methylene groups in the diolic unit.

containing saturated or aromatic rings have the highest glass transition temperatures: the increase follows the order N,N' -bis(2-hydroxyethyl)piperazine (BHP) < 1,4-cyclohexanedimethanol (CHM) < 1,4-benzenedimethanol (BDM) < bis(2-hydroxyethyl) terephthalate (BHT) < 1,2-cyclohexanediol (CHD) and is observed for both S/BO (Table 2) and S/PBO (Table 1) series. Glass transition temperatures range from 21 to 33 °C in the former case (the oxazoline is more flexible) and from 39 to 52 °C in the latter (more rigid 2-oxazoline). Attempts to prepare poly(ester-amide)s where all the three constituting comonomers are highly rigid, like BDM/F/PBO, failed because the temperatures attainable with the oil bath are not high enough to assure fluidity of the reaction mixture.

Polymers from $HO(CH_2)_nOH$ linear diols show a regular decrease of T_g from 66 °C ($n = 2$) to 20 °C ($n = 12$) with an increase in n for F/PBO series (Table 3). In S/PBO series (Table 1), the polymers with $n = 3, 4$, and 6 exhibit comparable glass transition temperatures. In S/BO series (Table 2) glass transition temperatures are situated in a narrow range from –2 to +7 °C and apparently very erratically. As previously pointed out, the polymer with $n \geq 4$ belonging to S/BO and S/PBO series exhibits a melting endotherm, at temperatures around 110 and 150 °C, respectively. The glass transition temperatures as a function of the number of methylene groups in the diolic unit are reported in Figure 3.

Polymers from $HO(CH_2CH_2O)_nH$ diols exhibit also a regular decrease of T_g with an increase in n in each series (Tables 1, 2, and 4); T_g values as a function of oxyethylenic groups in the diolic unit are reported in Figure 4.

Substitution of one or more hydrogen atoms of the diol with methyl groups leads to an increase in the stiffness of the alkylene moiety. Accordingly, using 1,2-propanediol (PG) instead of ethylene glycol (EG) (substitution of a hydrogen atom of the $-CH_2CH_2-$ group with a methyl group), the glass transition temperatures of the polymers vary from 5 to 11 °C (S/BO series; Table 2), from 32 to 34 °C (S/PBO series; Table 1), and from 66 to 79 °C (F/PBO series; Table 3).

By using neopentyl glycol (NPG) as the comonomer instead of 1,3-propanediol (PD) (two methyl groups in

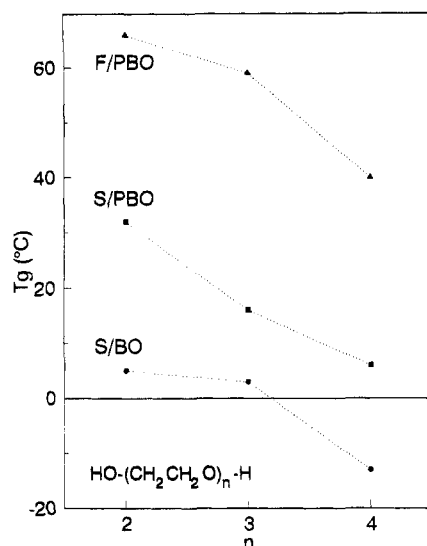


Figure 4. Glass transition temperatures of several series of poly(ester–amide)s as a function of the number of oxyethylenic groups in the diolic unit.

place of two hydrogen atoms of the central methylene of the $-\text{CH}_2\text{CH}_2\text{CH}_2-$ group), the glass transition temperatures increase from 7 to 18 °C (S/BO series; Table 2), from 22 to 30 °C (S/PBO series; Table 1), and from 58 to 72 °C (F/PBO series; Table 3). This behavior suggests that the two methyl groups are sterically hindered in their motion, since “free” methyl groups should lead to decreased glass transition temperatures.²⁷

As a final remark, the observed well-defined correlations prove that the molecular weights of the polymers are above the critical molecular mass for which an increase in T_g is observed,^{27,28} although very low inherent viscosities (<0.1 dL/g) were found for some samples of F/PBO series (Table 3).

Poly(ether–ester–amide)s from Mixtures of Ethylene Glycol and Poly(ethylene glycol). Block-segmented poly(ether–ester–amide)s can be prepared by using a dihydroxy-terminated polyether as a comonomer in place of the diol. From this point of view the polymerization reaction described in this paper seems particularly attractive, since many dihydroxy-terminated polyethers and polyesters are commercially available (used, for instance, in polyurethane synthesis), while the dicarboxy-terminated homologues are not.

Recently, preparations of block-segmented poly(ether–amide)s through step-growth polyadditions of bis(oxazolone)s and amino²⁹ or hydroxy-terminated³⁰ polyethers were reported by Acevedo et al. Furthermore, poly(ester–amide)s are potentially very interesting biodegradable materials;³¹ the incorporation of polyether segments into the polymer chain represents an advantageous method to enhance degradability.

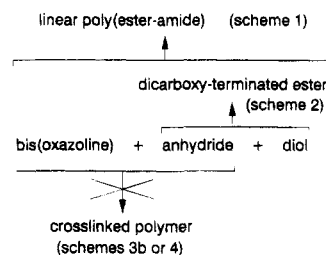
Thus, poly(ether–ester–amide)s with variable soft segment amounts were prepared by polymerization of PBO, S, and poly(ethylene glycol) (PEG) ($M_n = 2106$) or mixtures of PEG and ethylene glycol. In the latter case molar ratios PEG/EG in the range 5–30:95–70 were used. PEG was titrated prior to polymerization runs to determine the exact molecular weight and to be able to respect the reaction stoichiometry. Indeed, the molecular weights of PEG given by the supplier lie within a $\pm 10\%$ uncertainty range; besides it is known that the nominal molecular weights for PEG–monomethyl ether are sometimes unreliable.³²

Table 6. Characteristics of Poly(ester–amide)s from 2,2'-(1,4-Phenylene)bis(2-oxazoline), Succinic Anhydride, and Mixtures of Ethylene Glycol (EG) and Poly(ethylene glycol) (PEG, $M_n = 2106$)

sample	mole ratio PEG/EG	IV ^a (dL/g)	T_g (°C)	T_m (°C)
PE 100	100:0	0.48	–28	43
PE 30	30:70	0.30	–27	42
PE 10	10:90	0.34	–26	175
PE 5	5:95	0.31	–24	164

^a Inherent viscosity.

Scheme 8



Thermal characteristics of polymers are reported in Table 6. Only a single glass transition temperature is observed in all samples in the range -28 to -24 °C, attributed to the soft amorphous phase. PE 100 and PE 30 melt at 42–43 °C, while a melting temperature of about 170 °C is exhibited by the polymers with lower PEG content.

The possible presence of a second T_g (which would suggest incompatibility and probably should be found at around 30 °C; see EG/S/PBO; Table 1) is not detectable, since the melting peak is present in the thermogram of PE 30 and a crystallization exothermic peak upon heating appears in the same region for PE 10; the thermogram of PE 5 is free from interferences and flat, but in this case the hard/soft ratio is rather low. However, it is possible that the observed slight regular increase in T_g with the EG/PEG ratio may reflect the existence of some degree of compatibilization among polyether blocks and poly(ester–amide) blocks.

Conclusions

The attainment of linear polymers from bis(2-oxazoline)s, anhydrides, and diols was, in principle, not straightforward. Indeed, homopolymerization of bis(2-oxazoline)s or copolymerization of bis(2-oxazoline)s with anhydrides would lead to cross-linked resins.

However, it was found that the one-pot reaction between bis(2-oxazoline)s, anhydrides, and diols follows a simple path (Scheme 8) which leads to linear poly(ester–amide)s with ordered structures, as confirmed by NMR analyses.

Although it is difficult to exactly respect the ideal stoichiometric bis(2-oxazoline)/anhydride/diol ratio 1:2:1, polymers having inherent viscosities in the range 0.10–0.47 dL/g were obtained in most cases.

Glass transition temperatures are closely related to the polymer structure (length and stiffness of the diol monomer, presence of substituents, stiffness of 2-oxazoline, etc.). Melting temperatures (when present) are related to the structure of poly(ester–amide)s as well. In this way, it is possible to obtain a whole range of new thermoplastic polymers, whose properties can be easily tuned varying the comonomer feed.

Experimental Part

Monomers. All the diols and anhydrides (Fluka or Aldrich) were checked by NMR and IR and used without previous

purification. The other products were used as received. Poly(ethylene glycol) (Fluka) was titrated prior to use to establish its molecular weight.

2,2'-(1,4-Phenylene)bis(2-oxazoline) (PBO), 2,2'-bis(2-oxazoline) (BO), and 2,2'-(2,6-naphthylene)bis(2-oxazoline) (NBO) were prepared following general procedures reported in the literature.^{2,3,33} The two-step preparation of PBO is reported in detail as an example.

***N,N'*-Bis(2-hydroxyethyl)terephthalamide.** In a three-necked round-bottom flask fitted with a nitrogen inlet and a Claisen condenser, 97.0 g of dimethyl terephthalate (0.5 mol) was mixed under stirring with 180.0 g of 2-aminoethanol (3.0 mol); the mixture was heated at 120 °C for 1 h until methanol was distilled away. After 4 h of further heating, the mixture was cooled at room temperature and the excess of 2-aminoethanol was evaporated in vacuo. The product was recrystallized from water/ethanol (5:2) and dried in a vacuum oven at 80 °C to give 108.1 g of white needles (yield 85%) characterized by ¹H NMR.

2,2'-(1,4-Phenylene)bis(2-oxazoline) (PBO). To a three-necked flask fitted with a nitrogen inlet containing 400 mL of methylene chloride was added 43.2 g (0.176 mol) of *N,N'*-bis(2-hydroxyethyl)terephthalamide. A total of 68 mL (0.932 mol) of thionyl chloride was added dropwise to the mixture at 0 °C. After 24 h of stirring at room temperature, the product was filtered and cautiously added to a 5% NaHCO₃ aqueous solution under vigorous stirring. The precipitate was repeatedly washed with water, recrystallized from ethanol, and dried in a vacuum oven to give 34.8 g of white powder (yield 94%) characterized by ¹H NMR. Mp: 243–246 °C (lit.³⁴ mp 246 °C).

Polymerization Runs. The synthesis of the polymer from PBO, succinic anhydride (S), and 1,6-hexanediol (HD) [poly(iminoethyleneoxysuccinoyloxy-1,6-hexamethyleneoxysuccinoyloxyethyleneiminoterephthaloyl); HD/S/PBO] is described in detail. The other polymer samples were prepared in the same fashion. Reaction conditions of various runs are reported in Tables 1–4.

In a glass tube fitted with a nitrogen inlet were introduced 3.00 g (30 mmol) of succinic anhydride, 2.10 g (15 mmol) of PBO, and 1.77 g (15 mmol) of 1,6-hexanediol. The mixture was melted and heated in an oil bath at 150 °C under gentle mechanical stirring. The product became quickly a light brown viscous fluid. After 1.5 h the product was chilled and recovered.

Reaction between 2,2'-(1,4-Phenylene)bis(2-oxazoline) and Succinic Anhydride. In a glass tube fitted with a nitrogen inlet were introduced 4.003 g (40 mmol) of succinic anhydride and 4.325 g (20 mmol) of PBO. The mixture was melted and heated in an oil bath at 180 °C under gentle mechanical stirring. After about 5 min the brown liquid became suddenly a dark solid mass, insoluble in organic solvents.

Reaction between 2,2'-(1,4-Phenylene)bis(2-oxazoline) and Ethylene Glycol. In a glass tube fitted with a nitrogen inlet were introduced 7.450 g (120 mmol) of ethylene glycol and 2.162 g (10 mmol) of PBO. The mixture was heated at 200 °C for 5 h under stirring. NMR and GC analysis showed that the product consisted of the unreacted starting products.

Differential Scanning Calorimetry (DSC). DSC scans were performed with a Perkin-Elmer DSC 7 calorimeter, using indium for the temperature calibration. Each sample was heated at constant rate (20 °C/min), cooled (10 °C/min), and heated again (20 °C/min). Reported glass transition temperatures (*T*_g) were measured in the first heating scans. Melting temperatures were measured in the second heating scans.

Inherent Viscosities. Inherent viscosities (IV) were measured on 0.5 g/dL polymer solutions in *m*-cresol at 60 °C, using a Desreux-Bischoff viscosimeter.

Nuclear Magnetic Resonance. ¹H- and ¹³C-NMR spectra were recorded with a Bruker AM-300 spectrometer operating

at 75.469 MHz for ¹³C and 300 MHz for ¹H. Polymer samples were dissolved in DMSO-*d*₆. Chemical shifts were referred to tetramethylsilane (0.0 ppm).

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