ELSEVIER

European Polymer Journal 38 (2002) 229–233

EUROPEAN POLYMER JOURNAL

www.elsevier.com/locate/europolj

Poly(siloxaneimide)s 2. Polycondensation of some imidic diacid chlorides with aminoalkylsiloxanes

Mihaela Simionescu *, Mihai Marcu, Maria Cazacu, Carmen Racleş

"P. Poni" Institute of Macromolecular Chemistry, Aleea Gr. Ghica Vodă 41A, Iaşi 6600, Romania

Received 25 February 2001; received in revised form 3 May 2001; accepted 13 July 2001

Abstract

Some new poly(siloxaneimide) copolymers with good solubilities have been synthesized by solution polycondensation of aromatic diacid chlorides containing preformed imide rings with disiloxanes and siloxane oligomers having α,ω-aminopropyl functionalities. The polycondensation reactions were carried out using equimolecular amounts of the two monomers, in polar aprotic solvents and inert atmosphere.

The obtained compounds were characterized by elemental C, H, and Si analysis, solubility measurements, IR and ^{1}H-NMR spectrometry. Thermogravimetric curves were also recorded. All data agree with the proposed structures.

1. Introduction

A considerable number of siloxane-containing condensation polymers such as polyamides, polyimides and heterocyclic polymers has been reported, some of which showed good thermal stability and enhanced solubility in organic solvents [1].

Polyimides are perhaps the most important class of very high temperature polymers [2–4]. Whereas their thermal and oxidative stability, physical strength, softening temperature and solvent resistance are highly valued, these materials possess the serious disadvantage of being typically insoluble and unprocessable. One approach to solve this problem is to decrease the softening (glass) temperature of these polymers or to enhance their solubilities without affecting their high temperature stability and the other desired properties.

Incorporation of flexible siloxane segments into the polyimide backbone has been one means of enhancing solubility while still maintaining excellent high performance properties of the copolymer system [5]. The siloxanes impart a number of additional benefits to the polymeric system into which they are incorporated, including reduced water absorption, high gas permeability, good resistance to aggressive oxygen environments, modified surface properties, adhesive properties and improved flame resistance.

The poly(siloxaneimide) copolymers are generally synthesized from a combination of a dianhydride and diamine monomer and an aminoalkyl-ended polydimethylsiloxane to form the segmented polyamic acid [6–12]. The polyamic acid is then cyclodehydrated by either thermal or solution imidization to give randomly segmented poly(siloxaneimide) copolymers.

This paper presents another method to prepare novel imidesiloxane copolymers, which integrates our efforts to obtain new compounds with optimal properties between polyimides and polysiloxanes. This method presume a polycondensation reaction between functionalized siloxanes and certain compounds with reactive end groups and having preformed imide rings [13].

* Corresponding author.

E-mail address: msimionescu@ichpp.tuiasi.ro (M. Simionescu).

0014-3057/01/$ - see front matter
PII: S0014-3057(01)00184-7

2. Experimental

2.1. Materials

Oxy-bis-*N*(4-phenylene)-4′(chloroformyl)phthalimide (**IM**$_1$), methylene-bis-*N*(4-phenylene)-4′(chloroformyl)-phthalimide (**IM**$_2$) and sulfuryl-bis-*N*(4-phenylene)-4′(chloroformyl) phthalimide (**IM**$_3$) were prepared and purified according to Ref. [14]. Octamethylcyclotetrasiloxane, $[(CH_3)SiO]_4$ (D_4) was supplied by Fluka AG with 99% purity, m.p. = 17.5 °C, b.p. = 175 °C/760 mmHg, $n_D^{20} = 1.3962$, $d_4^{20} = 0.955$. 1,3-bis-(3-aminopropyl)tetramethyldisiloxane, $[H_2N(CH_2)_3(CH_3)_2Si]_2O$ (BATS) was purchased from SIGMA, with $d_4^{20} = 0.9$. Siloxane compounds were used as received. Tetramethylammonium hydroxide (TMAH) was supplied by Fluka. Dimethylacetamide (DMAc) was purified by distillation from a mixture of 250 g DMAc, 30 g benzene and 10 g water. First were distilled: benzene, water, amines and NH_3 and in the end, in vacuum, pure DMAc. Tetrahydrofurane (THF) was dried over sodium and freshly distilled. Triethylamine (TEA) was dried over NaOH for 24 h and freshly distilled before use.

2.2. Measurements

IR spectra were recorded on a Specord spectrophotometer using KBr pellets. Thermogravimetric analysis data were obtained on a Paulik Derivatograph in air at a heating rate of 9 °C/min. ^{1}H-NMR spectra were recorded on a JEOL spectrometer at 25 °C, using TMS as internal standard and DMSO as a solvent. Changes in optical textures of the samples during heating and cooling processes were examined using the polarizing optical microscope (POM) equipped with a hot stage in air. Intrinsic viscosities were determined at 25 °C, using Ubbelohde viscosimeter.

2.3. Procedure

2.3.1. Synthesis of aminopropyl-ended polydimethylsiloxane oligomers

Synthesis of α,ω-bis-(aminopropyl)polydimethylsiloxanes were performed through anionic ring-opening polymerization of octamethylcyclotetrasiloxane in the presence of 1,3-bis-(aminopropyl)tetramethyldisiloxane as chain transfer agent and tetramethylammonium hydroxide as catalyst.

In a reaction vessel, equipped with thermometer, mechanical stirrer and nitrogen inlet, the catalyst, used as 10% solution in methanol, was introduced. Then octamethylcyclotetrasiloxane and the amount of chain transfer agent necessary to obtain the desired molecular weights (1000 and 3000 g/mol) were added. The reaction mixture was stirred for 5 h, at 80 °C. In the end, the temperature was suddenly raised to 150 °C, for 1 h, in order to inactivate the catalyst, followed by distillation of unreacted monomers at 150 °C and 20 mmHg.

2.3.2. Polycondensation procedure

The siloxane copolymers were synthesized by solution polycondensation reactions of equimolecular amounts of diacid chlorides with preformed imide rings and disiloxane and siloxane oligomers having α,ω-aminopropyl functionalities. As a solvent we used DMAc when the reaction involved a disiloxane and a mixture of DMAc and THF for the siloxane oligomers. The polycondensations were run in anhydrous conditions, in nitrogen atmosphere.

A three-necked flask fitted with stirrer and drying tube was flushed with nitrogen and charged with siloxanic diamine compound and solvent to obtain a 10–20% final solution of polymer. The flask content was cooled with ice and the diacid chloride (as a finely divided powder) was added all at once with stirring. Then, the corresponding amount of triethylamine, as an acid acceptor, was added. The flask content was kept below 0 °C for 30 min then slowly raised to room temperature within other 30 min and kept at room temperature for 3 h. In the end, the triethylamine chlorhydrate was filtered and the polymer was precipitated by pouring into water. After filtration and drying, solid products with 72–75% yield were obtained.

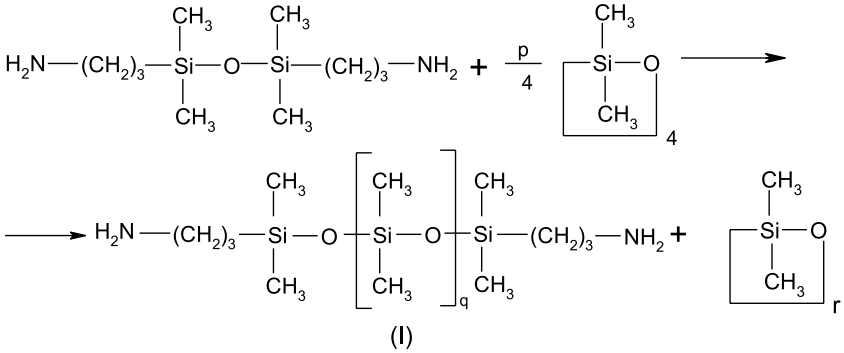
3. Results and discussion

Siloxane oligomers (**I**), with various molecular weights ($M_n = 1000$ and 3000 g/mol), were synthesized by equilibration of octamethylcyclotetrasiloxane with 1,3-bis(aminopropyl)tetramethyldisiloxane, at calculated molar ratio of comonomers (Scheme 1). This is an equilibrium reaction so, beside the corresponding oligomer, the final reaction mixture will also contain an amount of cyclosiloxanes. Therefore, q values, which indicate the numerical molecular weight of the oligomers were estimated from ^{1}H-NMR spectra, by measuring the integrated signals for the protons in CH_3 and CH_2 groups ($\delta = 0.15$ and 2.6–2.9 ppm, respectively).

Segmented poly(siloxaneimides) (**II**) were synthesized by direct polycondensation reactions, in solution, without catalyst, of some diacid chlorides having preformed imide rings (**IM**), with disiloxanes and siloxane oligomers having aminopropyl end-groups (Scheme 2).

Elemental analysis data and the inherent viscosities of the copolymers, determined in DMAc, at 25 °C, are presented in Table 1.

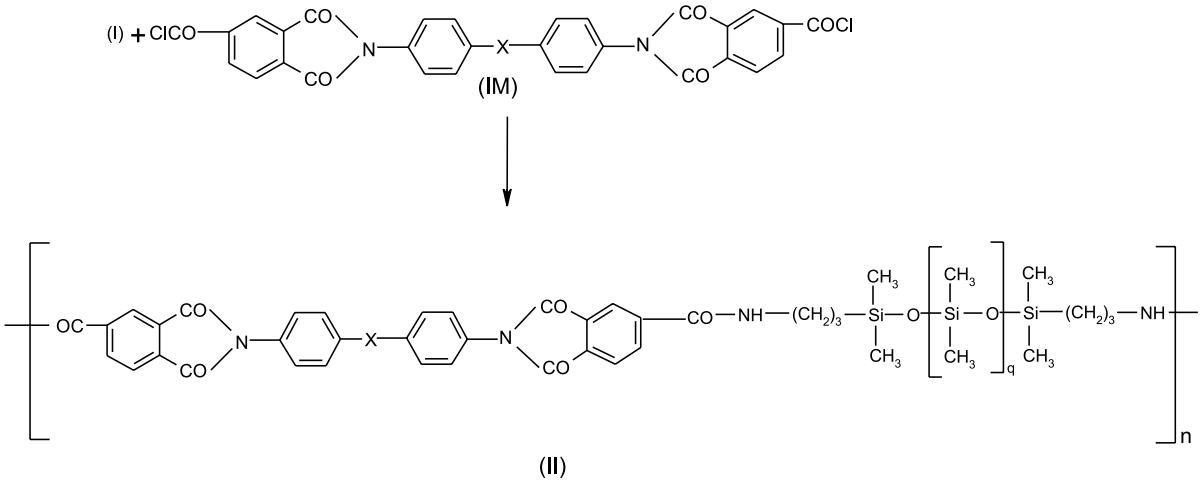
As we can see from Table 1, only small differences are noticed between the experimental and calculated elemental analysis data, probably due to an incomplete purification of the copolymers. The inherent viscosities of 0.16–0.34 dl/g, determined in DMAc, at 25 °C, are



(I)

q = 10, 35 ; r = 3, 4, 5….

Scheme 1.



(IM)

(II)

X = CH_2, SO_2, O

Scheme 2.

Table 1
Elemental analysis data and inherent viscosities of the copolymers

Code	q	X	%C		%H		%Si		$[\eta]$ (dl/g)
			Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	
IIa$_1$	0	CH_2	64.9	63.8	5.54	5.51	7.38	7.42	0.34
IIa$_2$	0	SO_2	59.4	58.5	4.95	4.88	6.93	7.00	0.29
IIa$_3$	0	O	63.1	62.9	5.26	5.22	7.36	7.38	0.31
IIb$_1$	10	CH_2	49.7	48.6	6.74	6.70	21.6	21.8	0.21
IIb$_2$	10	SO_2	47.2	47.1	6.37	6.31	20.8	20.9	0.23
IIb$_3$	10	O	48.8	47.9	6.59	6.42	21.5	21.9	0.21
IIc$_1$	35	CH_2	39.9	39.1	7.51	7.12	30.7	30.9	0.18
IIc$_2$	35	SO_2	38.9	37.8	7.34	6.98	30.2	30.6	0.16
IIc$_3$	35	O	39.5	40.1	7.45	7.32	30.7	31.1	0.16

reasonable for this kind of copolymers. Besides, these values of inherent viscosities are not quite comparable to the molecular weights of the copolymers because DMAc, the solvent for viscosity measurement, is a good

Table 2
The solubilities of the reactants and products

Sample	Solvent				
	Toluene (8.9)	THF (9.52)	NMP (11.17)	DMF (12.15)	DMSO (13.04)
(I)	+	+	−	−	−
(IM)	−	−	+	+	+
(II)	−	+	+	+	+

+ soluble; − insoluble. δ, the solvent solubility parameter [15] is given in parenthesis.

solvent for the organic part, but a poor solvent for polysiloxane. We can notice that for the copolymers having longer siloxane chains, the inherent viscosities values are lower.

The solubility tests results in various solvents of different polarities showed an improved solubility of the copolymers comparing to starting imidic products. Therefore, we can notice an extension in the range of solubility for the siloxaneimide copolymers, towards less polar solvents when comparing with imidic diacid chlorides, and towards high polar solvents when comparing with siloxane oligomers (Table 2). This improvement of the copolymer solubility is due to the decreased intermolecular interactions in the presence of linear flexible siloxane chains.

The IR spectra of the synthesized products show absorption bands that agree with the expected structures. The appearance of the Si–O–Si band at about 1020 cm^{-1}, the presence of the strong bands corresponding to imide rings at 1770–1780, 1710–1720, 715–720 cm^{-1} and also the appearance of the amidic bands **I**, **II** and **III** at 1670–1690, 1530–1560 and 1260–1280 cm^{-1} confirm that the polycondensation reaction took place (Table 3). The proposed structures were also confirmed by the chemical shifts in ^{1}H-NMR spectra (Fig. 1).

Table 3
Infrared absorption of copolymers

Experimental values (cm^{-1})	Literature values (cm^{-1})	Assignment
3300–3400	3440	N–H amidic
3090–3050	3000–3100	CH (aromatic)
2950–2930	2960	CH (aliphatic)
1780	1770–1780	$(CO)_2N$
1710	1710–1720	$(CO)_2N$
1670–1690	1680	CO–NH (amide I)
1610	1590	C=C (aromatic)
1530–1560	1530	CO–NH (amide II)
1390	1390	Si–CH_2
1260–1280	1260	CO–NH (amide III)
1250	1240–1280	Si–CH_3
1050–1100	1020–1100	Si–O–Si
760	780	Si–CH_3
720	715–720	$(CO)_2N$

The thermogravimetric curves, registered in air, at a heating rate of 12 °C/min, show a good thermal stability of the siloxane-imide copolymers, placed between those of the imides and siloxanes (Fig. 2).

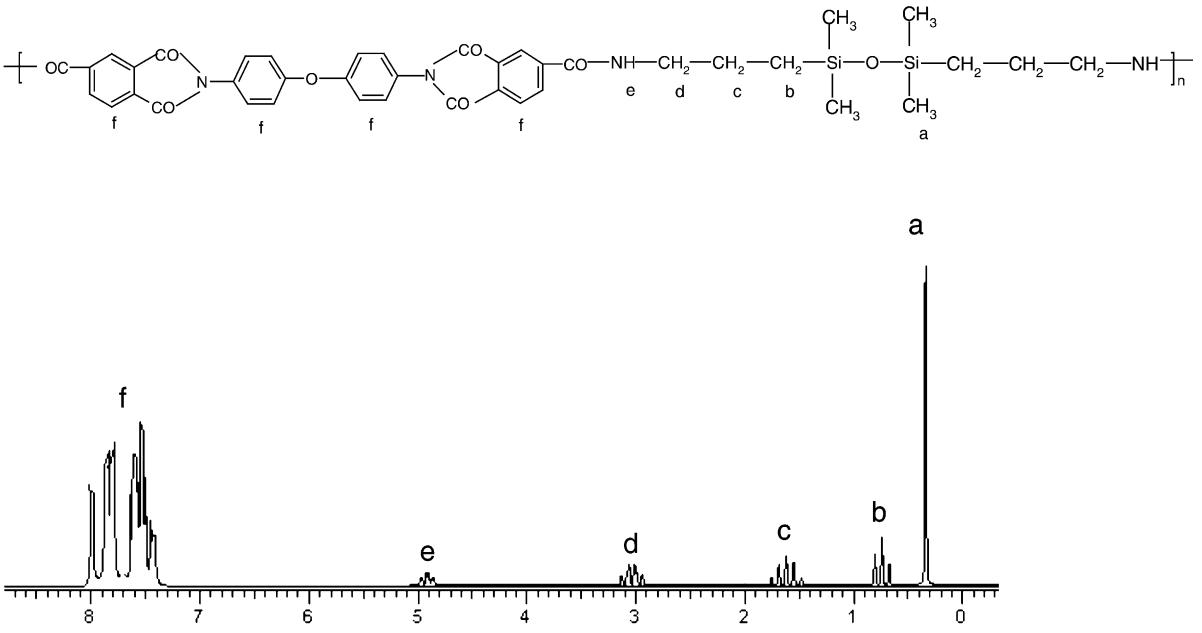


Fig. 1. The ^{1}H-NMR spectra of copolymer **IIa$_3$**.

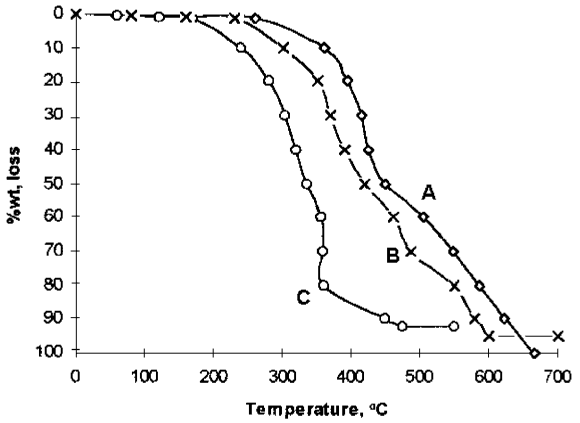


Fig. 2. TG curves in air for (A) $\mathbf{IIa_1}$, (B) $\mathbf{IIb_1}$ and (C) $\mathbf{IIc_1}$.

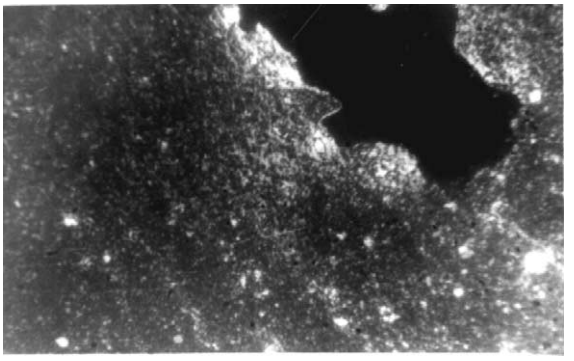


Fig. 3. POM microphotograph of copolymer $\mathbf{IIb_1}$.

In all cases, the thermal stability is very good. The copolymers are not decomposed under 300 °C. On the DTA curves, the onset of an exothermic reaction was observed around 300 °C. The exothermic reaction was due apparently to decomposition of polysiloxane units. This is supported by the TG curves, which reveal the copolymers to begin to lose weight above 300 °C in air. The temperature at which the decomposition begins depends on the copolymer structure, becoming lower when the siloxane is introduced. By increasing the length of the siloxane segment, the decomposition temperature decreases.

The microscopy observations (Fig. 3) showed phase separation in melt for all copolymers synthesized starting from siloxane oligomers. This behavior is somewhat surprising because phase separation is a common phenomenon for block copolymers. However, it was reported that a siloxane molecular weight as low as 500–600 g/mol and an organic segment having only a single structural unit is sufficient to obtain two-phase morphologies. Also, recent investigations on microdomains stated that when two incompatible monomers provide a copolymer molecule, the copolymer melt undergoes a spatial segregation due to the chemical interactions. Therefore we suppose that, probably, the phase separation observed for our samples could be due to the pronounced incompatibility between the hard units (aromatic imide) and the soft segments (aliphatic siloxane) [16]. As a result, a tendency of segregation on microdomains occurs.

4. Conclusions

Using a solution polycondensation technique, flexible siloxane segments were incorporated into a polyimide backbone. Reasonably high molecular weights were obtained. The obtained copolymers showed increased solubility towards the starting imide and better thermal stability compared with the siloxane.

Acknowledgements

This work was financially supported by National Agency for Science, Technology and Innovation (grant ANSTI 5052/1999-B5 Act additional no. 12633/26 VI 2000).

References

[1] Yilgor I. Adv Polym Sci 1988;86(1):1–86.
[2] Feger C, Khojasteh MM, McGrath JE. Polyimides: Chemistry materials and characterisation. Amsterdam: Elsevier; 1989.
[3] Mittal K. Polyimides: synthesis, characterisation and applications. New York: Plenum Press; 1984.
[4] Abadie MJM, Sillion B. Polyimides and other high-temperature polymers. Amsterdam: Elsevier; 1991.
[5] Arnold CA, Summers JD, Chen D, Chen YP, McGrath JE. Polym Preprints 1988;29(1):349.
[6] Bowens AD, Robertson MAF, Riffle JS. Polym Preprints 1998;39(1):569.
[7] Hedrick JL, Brown HR, Volksen W, Sanchez M, Plummer CJG, Hilbern JB. Polymer 1997;38(3):605.
[8] Furukawa N, Yuasa M, Yamada Y, Kimura Y. Polymer 1998;39(13):2941.
[9] Chen SH, Lee MH, Yuin Y. Eur Polym J 1996;32(12):1403.
[10] Lai JY, Lee MH, Chen SH, Shyu SS. Polym J 1994; 26(12):1360.
[11] Furukawa N, Yamada Y, Furukawa M, Yuasa M, Kimura Y. J Polym Sci A: Polym Chem 1997;35:2239.
[12] Rogers ME, Rodrigues D, Brennan A, Wilkes GL, McGrath JE. Contemp Top Polym Sci 1992;7:47.
[13] Simionescu M, Marcu M, Cazacu M, Hamciuc E, Racles C, Sacarescu G. Revue Roumaine de Chimie 1999; 44(6):613.
[14] Bruma M, Neamtu G. Revue Roumaine de Chimie 1981;26(1):87.
[15] Hansen CM. Ind Chem Prod Res Dev 1969;8:2.
[16] Racles C, Cozan V, Marcu M, Cazacu M, Vlad A. Eur Polym J 2000;36:1951.