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New siloxane–ester modified polysulfones by phase transfer catalysis

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Abstract

Chemical modification of a chloromethylated polysulfone was performed by using siloxane-containing aliphatic carboxylic salts as modification agents and phase transfer catalysis. The obtained substitution degrees ranged between around 0.1 and 0.9, as determined by ^{1}H NMR, IR and elemental analyses. The introduction of siloxane–aliphatic moieties induced a decrease in the glass transition temperature (T_g) values of the obtained products in comparison to the starting polysulfone. All the modified polysulfones showed phase separation in optical microscopy. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Siloxane; Chloromethylated polysulfone; Phase transfer catalysis

1. Introduction

The preparation of polymers carrying various functional groups has received much attention since they can be used in a large variety of applications as supports, reagents or catalysts for various reactions [1].

Modified polysulfones have been prepared [2–7] by chemical transformations leading to coatings, membranes, selectively permeable films, ion-exchange fibers and resins etc.

The polysiloxane–polysulfone reaction systems have been studied widely in the last decades in order to obtain block-copolymers with valuable properties derived from their dual structure [8–18].

It is known that the incompatibility (and mostly the large difference between the solubility parameters of the organic and siloxane moieties) favors the biphasic morphology of the copolymers, which plays an important role in designing their properties [19,20].

On this subject the interest was mainly focused on polysiloxane–polysulfone block copolymers, in which phase separation was reported to occur at relatively low molecular weights of the blocks [10,21]. In our previous work [22], we noticed biphasic morphology at segmented siloxane–arylidene sulfone copolymers.

The present study had at least three purposes:

- to synthesize new modified polysulfones with pendant siloxane–aliphatic groups and carboxyl functionalities;
- to apply phase transfer catalysis on the polysulfone–disiloxane system; and
- to observe the morphology of the obtained products in order to establish, if possible, a minimum limit of siloxane content at which the phase separation occurs.

Phase transfer catalysis (PTC) is a very interesting approach in organic and polymer synthesis [23–28]. In order to react 1,3-bis(sebacomethyl)tetramethyldisiloxane with chloromethylated polysulfone, we used a dipotassium carboxylic salt which is only water-soluble, so that the most convenient reaction path seemed to be PTC.

2. Experimental

2.1. Materials

1,3-Bis(sebacomethyl)tetramethyldisiloxane was synthesized from 1,3-bis-(chloromethyl)tetramethyldisiloxane (ABCR), according to the method described in Ref. [29]. Its potassium salt (DSX1) was prepared by titration with 0.1 N KOH solution. Sebacomethylpentamethyldisiloxane was synthesized similarly, starting from chloromethylpentamethyldisiloxane (ABCR), which was then titrated to obtain DSX2. Polysulfone UDEL-P1700 (Union Carbide) is a commercial product which was chloromethylated following the procedure described in Ref. [7]. Phase transfer catalysts: benzyltrimethyl-ammonium chloride (BTMAC) from Merck was vacuum dried on P_2O_5 at room temperature; benzyldimethyl-lauryl-ammonium chloride

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Table 1
Reaction conditions

Code	Time (h)	PSF/DSX1[a]	Catalyst	Code	Time (h)	PSF/DSX1[a]	Catalyst
P1	24	1/2.18	–	P8	20	1/4	BDMLAC[b]
P2	24	1/3	CE	P9	20	1/4	BDMLAC
P3	24	2/1	BTMAC	P10	20	1/4	BDMLAC[c]
P4	8	1/3	BTMAC	P11	24	1/1[d]	–
P5	24	1/2.18	BTMAC	P12	24	1/1[d]	CE
P6	24	1/3	BTMAC	P13	24	1/1[d]	BTMAC
P7	24	1/3	BDMLAC	P14	24	1/1[d]	BDMLAC

[a] Molar ratio chloromethyl/DSX (for P1–P7, P9, P11–P14, molar ratio chloromethyl/catalyst = 1/1).
[b] Molar ratio chloromethyl/catalyst = 1/0.5.
[c] Molar ratio chloromethyl/catalyst = 1/2.
[d] DSX 2.

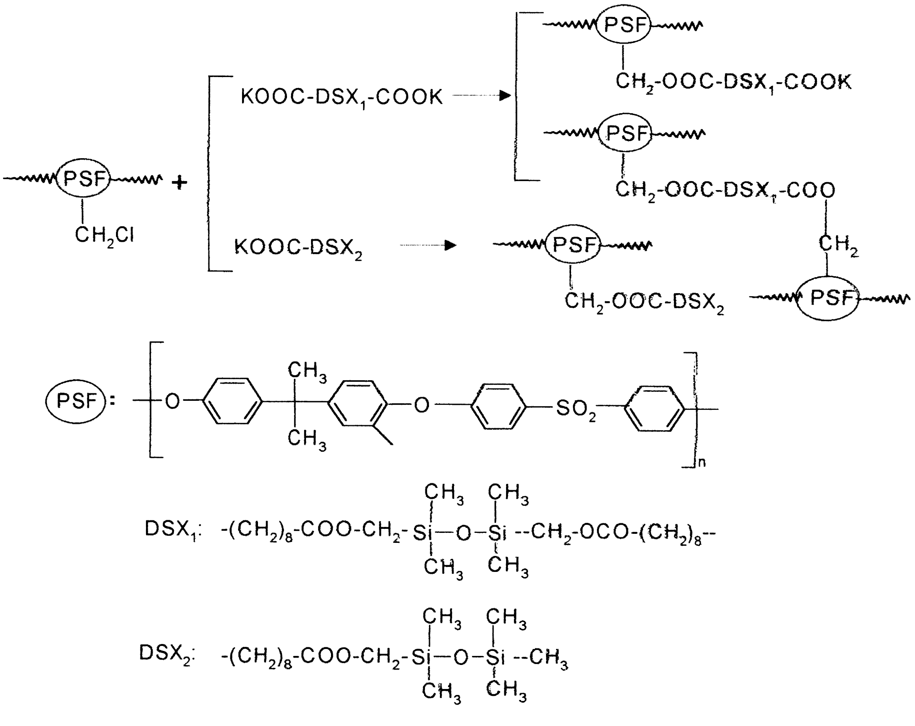
(BDMLAC) (Merck) and dibenzo-18-crown-6 (CE) (Fluka) were used as received.

2.2. Measurements

The IR spectra were recorded on a Specord M80 Carl Zeiss Jena spectrophotometer using KBr pellets. ^{1}H NMR spectra were registered on a Jeol 60 spectrometer using $CDCl_3$ as the solvent, without internal reference for the modified polysulfones and using TMS as the internal reference for the unmodified ones. Thermogravimetric curves were obtained in air with an F. Paulik Derivatograph at a heating rate of 12°C/min. The DSC analyses were performed on a Mettler TA DSC 12E Instrument. The phase separation behavior was monitored using an IOR MC1 type polarized optical microscope equipped with a heating stage.

2.3. Synthesis method (general procedure)

In a reaction vessel, thermostated at 50°C, an aqueous solution (2.5 wt%) of 1,3-bis(sebacomethyl)tetramethyldisiloxane potassium salt (DSX1) was placed. The catalyst (BTMAC or BDMLAC) was added in a stoichiometric amount with respect to the chlorine content of polysulfone, and dissolved. The chloromethylated polysulfone (PSF) (with 7.40% Cl) in chloroform (2.5 wt%) was then added dropwise and the reaction mixture was mechanically stirred. Details of the synthesis conditions and stoichiometry are given in Table 1. When CE was used, it was dissolved in the organic phase.



Scheme 1.

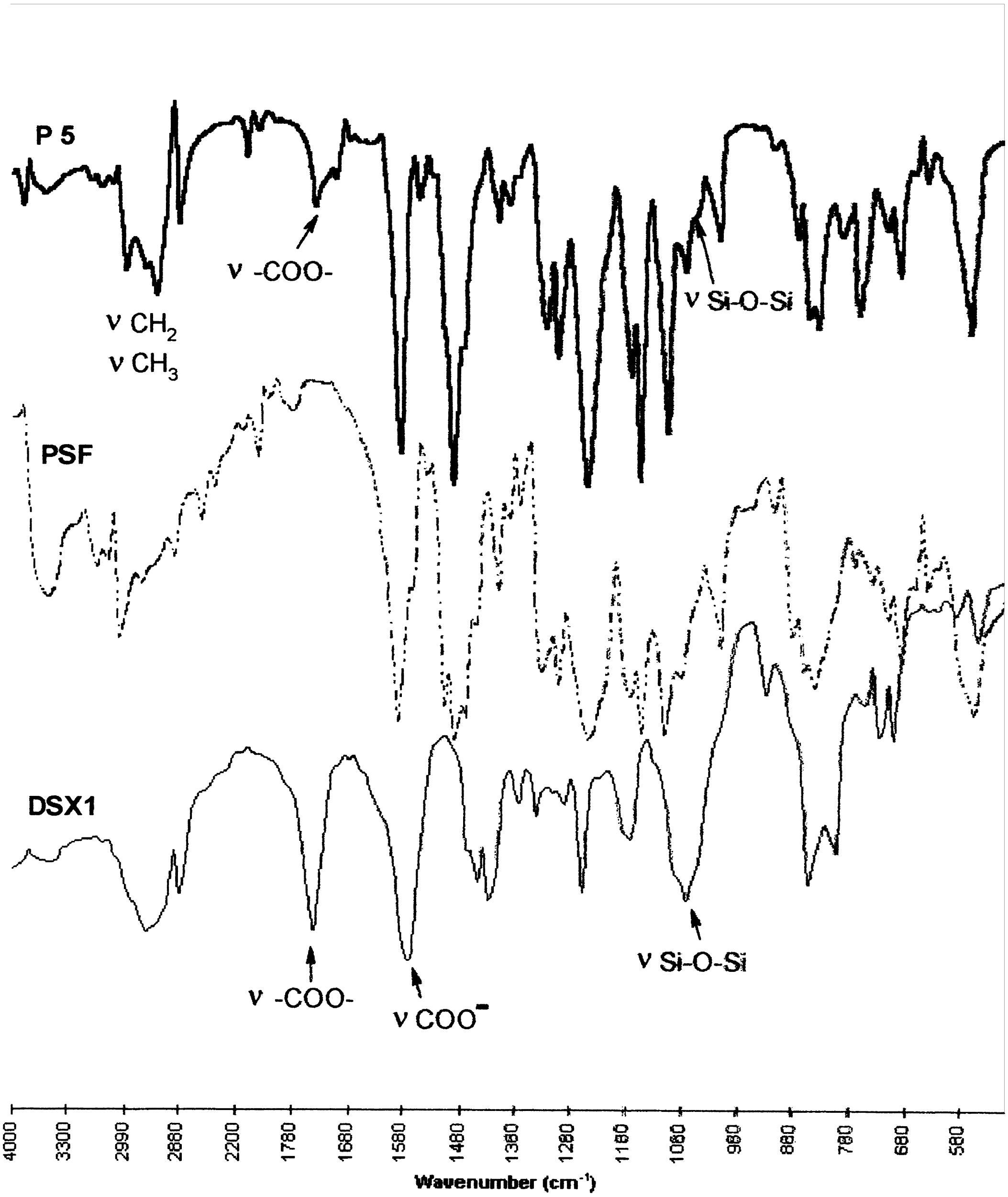


Fig. 1. The IR spectra of starting chloromethylated polysulfone (PSF), sebacomethyldisiloxane (DSX1), and modified polysulfone (P5).

After the reaction time expired, the mixture was allowed to separate, the organic phase was isolated and washed several times with water, then the product was precipitated with acetone, filtered and dried in vacuum at room temperature for 10 h. For optical microscopic observations, films were cast from chloroform. The analyses (^{1}H NMR, IR) were done as soon as the samples were prepared, since we observed crosslinking processes occurring with time due to the incomplete reaction of CH_2Cl and –COOK functionalities. In order to allow subsequent utilization in soluble state, transformation of the carboxylic salt functionalities into acid (by acidification) were performed.

3. Results and discussion

So far, in the reviewed literature concerning the polysulfone–siloxane system, there is no mention about the chemical modification of polysulfones with pendant siloxane–aliphatic groups.

New siloxane–ester modified polysulfones were obtained according to Scheme 1, starting from a chloromethylated polysulfone with 7.4% Cl, and the potassium salts of two sebacomethyldisiloxanes, DSX 1 and DSX 2. The initial polysulfone substitution degree (SD), i.e. the number of functional groups contained in the structural unit, was 1.025.

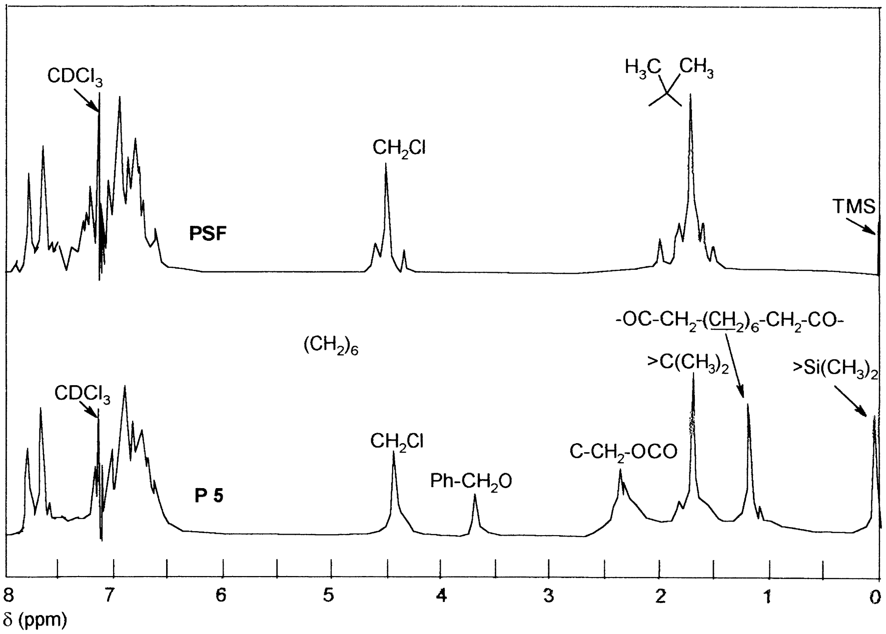


Fig. 2. The ^{1}H NMR spectra of chloromethylated polysulfone (PSF) and modified polysulfone (P5).

The ^{1}H NMR and IR spectrometry, as well as the elemental analyses (Cl%, Si%) were used to confirm the structure of the products and to estimate the substitution degree.

As one can see (Fig. 1), the IR spectrum of a reaction product (P5) shows the specific absorption bands for the expected structure. The most important evidence for the formation of new pendant moieties is the occurrence of the absorption band at 1740 cm^{-1} due to the stretching vibrations of the –COO– groups. Also, the aliphatic region from 2980 to 2820 cm^{-1} is modified in comparison with the starting polysulfone due to the stretching vibrations of the –CH$_2$– groups introduced. Finally, the presence of a shoulder at 1050 cm^{-1} was assigned to the stretching vibrations of the Si–O–Si groups.

The ^{1}H NMR spectrum of P5 (Fig. 2) shows the presence of all types of protons from the modified polysulfone. ^{1}H NMR spectra were used for SD calculations using the following formula:

$$\mathrm{SD} = \frac{A_2}{nA_1} \qquad (1)$$

where $n = 2$ for DSX1; $n = 2.5$ for DSX2; A_1 is the

Table 2
The substitution degree, catalyst type and chlorine content of the siloxane-ester-modified polysulfones (P1–P14)

Code	Catalyst	Substitution degree (SD)				Cl (%)[a]
		^{1}H NMR	IR	Elemental analysis	TGA	
DSX 1						
P1	–	0.08	0.10			7.10
P2	CE	0.12	–			7.06
P3	BTMAC	Cross-linked	–	0.15	0.17	–
P4	BTMAC	0.10	0.10		0.14	6.72
P5	BTMAC	0.20	0.17			5.94
P6	BTMAC	0.22	0.25			5.82
P7	BDMLAC	Cross-linked	–	0.69		2.75
P8	BDMLAC	0.28	0.30			5.61
P9	BDMLAC	0.52	0.54			3.75
P10	BDMLAC	Cross-linked	–	0.86		–
DSX 2						
P11	–	0.02	0.02			7.18
P12	CE	0.04	0.03			–
P13	BTMAC	0.05	0.06			7.15
P14	BDMLAC	0.32	–			5.07

[a] The initially chlorine content was 7.4%.

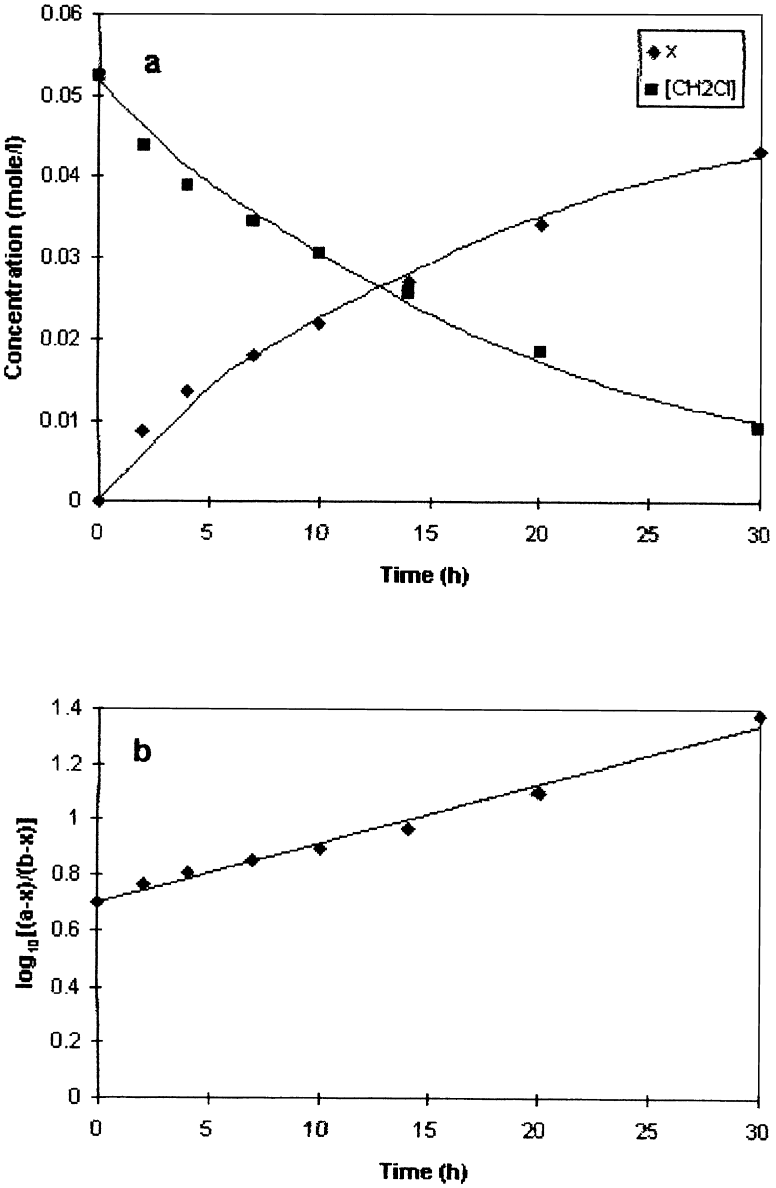


Fig. 3. The plot of kinetic data: (a) the variation of molar concentration of unreacted (CH_2Cl) and reacted (x) groups versus time; and (b) the variation of logarithmic ratio for unreacted reagents with time.

integrated area of the peak corresponding to $>C(CH_3)_2$ (6H); and A_2 is the integrated area of the peak corresponding to $>Si{-}CH_3$ (12H, DSX1; 15H, DSX2).

SD was also estimated from the IR spectra, considering the ratio A_{COO}/A_{1250} as a measure of the chemical transformation. The absorption band at 1250 cm^{-1} (considered as the reference) is assigned to the stretching vibrations of the C–O–C group in polysulfone and to deformation vibrations of the $Si{-}CH_3$ group in the siloxane units. The absorbances were calculated according to Ref. [30], taking a base line from 930 to 1850 cm^{-1}, free of any absorption.

As shown in Table 2 good correlations were observed between the two methods. The higher the reacted amount of chlorine, the higher the SD values.

For the cross-linked products (P3, P7, P10), the SD was estimated from Si% determinations, and/or TGA residue (considering the product as totally cross-linked).

As can be seen from Table 2, the most efficient catalyst was BDMLAC, since under the same reaction conditions, the SD for P7 (with BDMLAC) was almost three times higher than that of P6 (with BTMAC). The higher catalytic effect is also proved by the fact that P7 is a crosslinked product, while P6 is soluble. This was somewhat expected because the lauryl group is compatible with the sebacoyl one. CE had the weakest catalytic effect, probably due to its insolubility in the aqueous phase, and hence the difficulty of forming a catalytic complex with the potassium salt.

The same catalytic activity (BDMLAC $\gg$ BTMAC $>$ CE) was noticed in the case of samples P11–P14, where the crosslinking is avoided due to the siloxane structure.

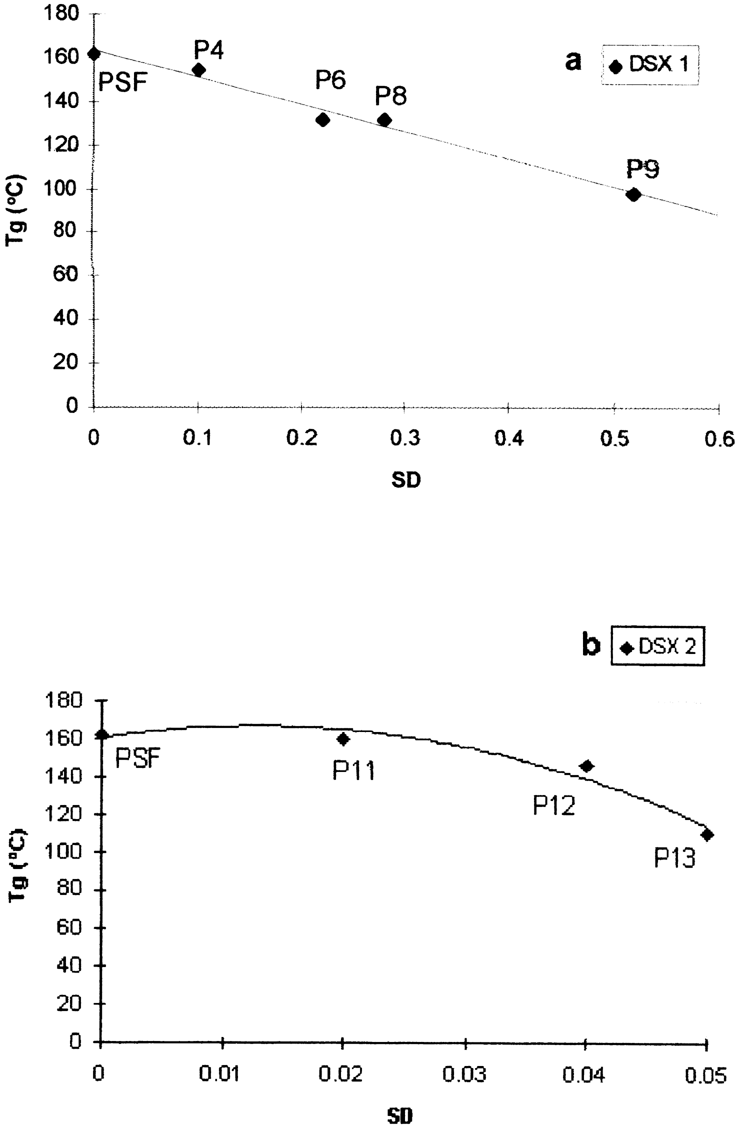


Fig. 4. The decrease of T_g with SD: (a) DSX1 series; and (b) DSX2 series.

By increasing the catalyst amount (samples P8–P10), an increase in SD values was noticed, and so also a higher tendency for crosslinking.

The molar ratio chloromethyl/DSX is also a very important factor, not only from the SD point of view, but also for preventing the crosslinking reactions. A molar ratio of 1/4 was considered sufficient to obtain soluble products, by using BDMLAC as the catalyst (molar ratio chloromethyl/catalyst, 1/1). However, to be sure, in the kinetic experiments a molar ratio of 1/5 was taken.

A kinetic study was run by ^{1}H NMR with BDMLAC as the catalyst and using a chloromethyl/DSX1 molar ratio of 1/5 at 50°C. Samples were withdrawn by a syringe, both from the organic and aqueous phases in corresponding amounts in order to maintain stoichiometry. A suggestive plot of the kinetic data is shown in Fig. 3a. All samples were soluble products.

We considered the reaction between a chloromethylated polysulfone and the siloxane carboxylic salt as a bimolecular, second-order one, with different initial concentrations of the reactants. The kinetic equation for such reactions is given as [31]

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k(a-x)(b-x) \tag{2}$$

where a and b are the initial molar concentrations of the starting compounds; x is the conversion variable.

The integrated form of the rate expression is

$$\log_{10}\frac{a-x}{b-x} = \log_{10}\frac{a}{b} + 0.434(a-b)kt \tag{3}$$

By plotting the $\log_{10}(a-x)/(b-x)$ values versus time (Fig. 3b), the rate constant k was calculated from the

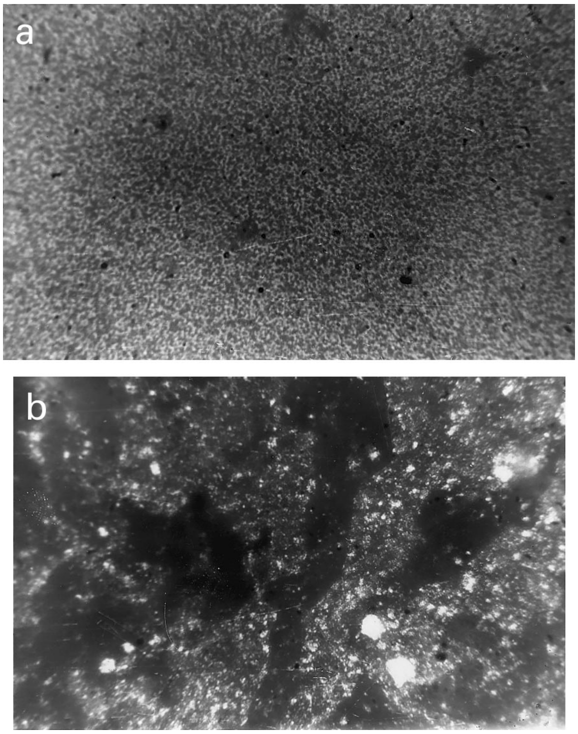


Fig. 5. Optical microphotographs of samples (magnification 150 ×): (a) P1; and (b) P2.

slope, using the following expression:

$$k = \frac{tg\alpha}{0.434(a-b)}; \qquad k = 1.154 \times 10^{-6}\ (\mathrm{l\ mol^{-1}\ s^{-1}}) \tag{4}$$

The T_g values of the obtained products were determined by DSC. As can be seen from Fig. 4a and b, the decrease of T_g reflects the plastification effect of siloxane-aliphatic segments, even at very small SD values. This effect is stronger with the increase of siloxane content.

The morphology of the products was evidenced by optical microscopy (magnification 150 ×) on films cast from chloroform. All the siloxane-modified polysulfones showed phase separation, irrespective of the SD (Fig. 5). Hence, the establishment of a "critical" content of siloxane at which phase separation occurred was not possible. A thorough study on this issue will be done in the near future by electron microscopy measurements.

References

[1] Mathur NK, Williams RE. J Macromol Sci: Rev Macromol Chem 1976;15:117.
[2] Daly WH. J Macromol Sci Chem A 1985;22:713.
[3] Arnold C, Assink R. J Membr Sci 1988;38:71.
[4] Arnold C, Assink R. Polymer 1989;30:1137.
[5] Guiver MD, Apsimov JW, Kutomy O. J Polym Sci: Polym Lett Ed 1988;26:123.
[6] Daly WH, Wu SJ. In: Culbertson BV, editor. Modification of polymers, Washington, DC: American Chemical Society, 1983.
[7] Avram E, Butuc E, Luca C, Druta I. J Macromol Sci, Pure Appl Chem A 1997;34(9):1701.
[8] Noshay A, Matzner M. Angew Makromol Chem 1973;37:215.
[9] Matzner M, Noshay A, Robeson LM, Merriam CN, Barclay R, McGrath JE. Appl Polym Symp 1973;22:143.
[10] Noshay A, Matzner M, Merriam CN. J Polym Sci: Part A-1 1971;9:3147.
[11] Collyer AA, Cleg DW, Morris M, Parker DG, Wheatley GW. J Polym Sci: Part A 1991;29:193.
[12] Butuc E, Cozan V, Giurgiu D, Mihalache J, Yushan N, Mengxian D. J Macromol Sci Pure Appl Chem 1994;A31(2):219.
[13] Di Pasquale G, La Rosa A, Mamo A. Macromol Chem Rapid Commun 1997;18(4):267.
[14] Noshay A, McGrath JE. Block copolymers: overview and critical survey. New York: Academic Press, 1977.
[15] Auman BC, Percec V. Polym Prepr 1986;27(1):320.
[16] Nagase Y, Mori S, Matsui K. Polymer 1989;30:1931.
[17] Wu J, Auman B, Schneider H, Canton H-I, Percec V. Makromol Chem Rapid Commun 1986;7(5):303.
[18] Gagnebien D, Madec P, Marechal E. Eur Polym J 1985;21(3):289.
[19] Yilgor I, McGrath JE. Adv Polym Sci 1988;86:1.
[20] Raigorodskii IM, Rabkin VS, Kireev VV. Vysokomol Soed 1995;37(3):445.
[21] Tyagi D, McGrath JE, Wilkas GL. Polym Engng Sci 1986;26(20):1371.
[22] Racles C, Cozan V, Marcu M, Cazacu M, Vlad A. Eur Polym J 2000 (in press).
[23] Frechet JMJ, Smet MD, Farrall MJ. J Org Chem 1979;44:1774.
[24] Gerbi DJ, Williams RF, Kellman R, Morgan JL. Polym Prepr 1981;22(2):385.
[25] Kellman R, Gerbi DJ, Williams JC, Williams RF. Polym Prepr 1982;23(1):174.
[26] Percec V, Nava H, Rodriguez-Parada JM. J Polym Sci: Polym Lett Ed 1984;22(10):523.
[27] Percec V, Nava H. Makromol Chem Rapid Commun 1984;5(6):319.
[28] Hurduc N, Scutaru D, Barboiu V, Vizitiu D, Simionescu CI, Buisine JM, Daoudi A. J Macromol Sci, Pure Appl Chem 1996;A33(11):1745.
[29] French Patent, 1955, 1,124,823.
[30] Jan F, Rabek E. Experimental methods in polymer chemistry. New York: Wiley, 1980 (p. 241).
[31] Isac V, Hurduc N. Chimie fizică. Cinetică chimică şi cataliză. Chisinău: Stiinta, 1994 (p. 32).