Polymer Bulletin 59, 873–882 (2008)
DOI 10.1007/s00289-007-0838-x

Polymer Bulletin

Non-Shrinking Polycyclocarbosiloxane Networks

Liviu Sacarescu (✉)

Institute of Macromolecular Chemistry “Petru Poni”, Aleea Grigore Ghica Voda 41A, 700487
Iasi, Romania
E-mail: livius@icmpp.ro; Fax: +40 232 211299

Received: 8 February 2007 / Revised version: 2 September 2007 / Accepted: 3 September 2007

Summary

Polycarbosiloxane networks were obtained by the anionic ring-opening polymerization of a cyclo-linear structure enclosing 2,7-dimethyl-3,3,6,6-tetraphenyl-1-oxa-2,7-disilacycloheptane segments in solvent free conditions. This precursor was prepared through the catalytic addition of 2,7-dimethyl-2,7-dihydro-3,3,6,6-tetraphenyl-1-oxa-2,7-disilacycloheptane to a poly(dimethyl-co-methylvinyl)siloxane oligomer. This method provides a non-shrinking highly cross-linked hybrid organic-inorganic material. Spectral analyses, TGA and DSC, were performed in order to investigate the structure of intermediates and of the product.

Introduction

The properties of the inorganic polymers can be modified by the introduction of organic groups into the inorganic framework [1]. One of the well known methods is the polymerization of molecular building blocks containing an organic fragment attached by nonhydrolizable carbon-silicon bonds to two or more trifunctional silyl groups. A classical example is the sol-gel polymerization of the tetraalkoxysilanes generating bridged polysilsesquioxane [2]. This widespread procedure has the inconvenient of an important shrinkage of the final products due to the loss of alkoxy groups. The shrinkage could attain up to 95% during air-drying of the gels and produces cracks on the resulted xerogels. This disadvantage could be eliminated through various methods such as the supercritical drying or by “solvent-free” polymerizations with mixtures of tetralkoxysilane, water, and catalyst [3-5].

Other examples are the free radical or ring-opening metathesis polymerization reactions of modified alkoxide monomers [6-13]. In these cases there is no emission of volatile organics but this does not compensate the shrinkage induced by the high density packing through covalent bonds between monomers.

Further attempts to reduce shrinkage were made by using ring-opening polymerization of cyclic monomers such as cyclic ethers [14], epoxides, [15, 16] and spirocarbonates [17]. Because the obtained products are oils or tacky solids they are unusable for gels preparation.

This work presents an experimental path to obtain non-shrinking new polycarbosiloxanes structures by anionic ring-opening polymerization of a specially designed liquid cyclocarbosiloxane precursor in solvent free conditions.

Experimental

Materials

Hexachloroplatinic acid, $H_2PtCl_6.6H_2O$ solution in isopropyl alcohol (HCPA) and octamethylcyclotetrasiloxane (99 % purity, GC) were purchased from Fluka. Tetrabutylammonium hydroxide (TBAH) (1M in methanol) was obtained from Sigma-Aldrich.

Tetramethyltetravinylcyclotetrasiloxane (V_4) was prepared in laboratory according to a previously established procedure [18].

$C_{12}H_{24}O_4Si_4$, Mw = 344.66. Elemental analysis: C 41.82% (C_{exp} 41.76%); H 7.02% (H_{exp} 6.89%); O 8.57% (O_{exp} 8.33%); Si 32.59% (Si_{exp} 32.64%).

Bp= 111°C/10mmHg; n_D^{20}= 1.4343; d_4^{20}= 0.9862

Hexamethyldisiloxane (HMDS) (99% purity, GC) and octamethylcyclotetrasiloxane (D_4) (99% purity, GC) supplied by Fluka were dried on molecular sieves and freshly distilled before use.

Cyclocarbosiloxane synthesis was done following the procedure of Sacarescu et al. [19]:

2,7-dimethyl-3,3,6,6-tetraphenyl-1-oxa-2,7-disilacycloheptane (HTFB)

$Si_2C_{30}H_{32}O$ (464/ 473_{exp}): 12.06/ 11.89_{exp} (Si%); 77.58/ 77.41_{exp} (C%); 6.89/ 6.77_{exp} (H%). Mp= 98.6°C.

^{1}H-NMR ($CDCl_3$, δ ppm): 0.14, 6H (Si-CH_3) ; 2.30, 4H, (-CH_2-); 4.85, 2H Si-H; 7.08-7.25, 20H, (-C_6H_5).

^{13}C-NMR ($CDCl_3$):- 6.8 (-Si-CH_3); 31.8 (-CH_2-); 34.8 (-C-); 126.3-129.3 (-Si-C_6H_5).

Polydimethylvinylsiloxane synthesis was made by the catalytic ring-opening polymerization of a D_4/V_4 cyclosiloxanes mixture with a known molar ratio, and HMDS as molecular weight regulator [20]. By employing this method poly(dimethyl-co-methylvinyl)siloxane oligomers (PDMVS) with controlled molecular weights and composition were obtained:

P1, Mw = 2600 g.mol^{-1} with 11.06% methylvinylsiloxy units, (MVS, ^{1}H-NMR);

P2, Mw = 5200 g.mol^{-1}, 12.10% MVS;

P3, Mw = 2300 g.mol^{-1}, 18.02% MVS;

P4, Mw = 4800 g.mol^{-1}, 21.04% MVS.

The spectral analyses of these oligomers show the following structural characteristics:

^{1}H-NMR ($CDCl_3$, δ, ppm): 0.3, -Si-CH_3; 6.01, -Si-CH=CH_2.

^{13}C-NMR ($CDCl_3$, δ, ppm): 0.97 –Si-CH_3; 140.3, 147.5 –Si-CH=CH_2.

IR (λ, cm^{-1}): 2900, CH (alkyl); 1600, 1405, –CH=CH_2; 1250, -Si–CH_3; 1100, -Si-O-800 -Si–CH_3.

Instruments

^{1}H-NMR and ^{13}C-NMR spectra were obtained on a JEOL 80 MHz spectrometer without internal standard and $CDCl_3$ as the solvent.

IR spectra were recorded on a Perkin-Elmer spectrophotometer in the 400-4000 cm^{-1} region using KBr pellets.

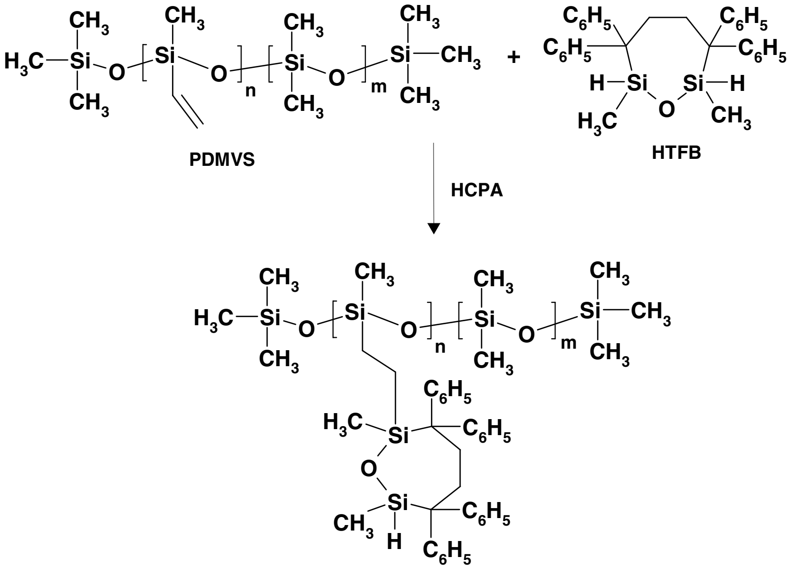
Gel permeation chromatography (GPC) experiments were carried out in toluene 1% solution at 30°C, with a flow rate of 1cm^3/min. on a Spectra Physics 8800 gel permeation chromatograph equipped with two PL-gel packed columns (10^{3}Å and 500 Å). An UV116 spectrometer and a R132 differential refractometer were used as detectors.

Viscosimetric measurements were performed employing an Ubbelohde viscosimeter using 2% solutions in dried toluene.

Thermogravimetric (TGA and DTG) analysis was performed on a MOM Paulik-Paulik-Erdey derivatograph. The samples were exposed to air at a heating rate within 9-12°C/ min.

Differential scanning calorimetry (DSC) measurements were carried out in a Mettler DSC12E calorimeter at a heating rate of 10°C/ min., in air.

Synthesis of the cyclo-linear carbosiloxane precursors (PCS$_{1-4}$). A Si-H cyclocarbosiloxane/ polydimethylvinylsiloxane mixture (1.3/ 1 molar ratio, 10% solution in 50 ml anhydrous n-heptane), was added under dry inert atmosphere in a 250 ml reaction flask. This mixture was heated to gentle reflux and then, a 0.01 N solution of hexachloroplatinic acid in isopropyl alcohol (5.10^{-6}g H_2PtCl_6/ mole compound with vinyl groups) was added [21]. The reaction was considered to be completed when the intensity of the 2150 cm^{-1} Si-H IR absorption band remained constant. (Reaction Scheme 1).



Scheme 1. Synthesis of the cyclo-linear carbosiloxane precursor

Subsequently, the solvent was distilled under vacuum and the catalyst and cyclocarbosiloxane excess was separated by ultracentrifugation. The resulted viscous liquid product was vacuum dried overnight.

Using the previously prepared P_{1-4} structures, four liquid precursors were obtained. Spectral analysis revealed their structural characteristics [22].

^{1}H-NMR ($CDCl_3$, δ, ppm) (Fig.1): 0.08, Si-CH_3; 0.6, -CH_2 (bridge); 2.3, -CH_2 (cycle); 4.85, -Si-H; 7.25, -C_6H_5.

^{13}C-NMR ($CDCl_3$, δ, ppm): - 6.8, -Si-CH_3 (cycle); 0.97, -Si-CH_3; 11.2, 14.8, -CH_2-(bridge); 31.8 (-CH_2-); 34.8 (-C-);126.3, 128.3, 129.3, 143.0 –C_6H_5.

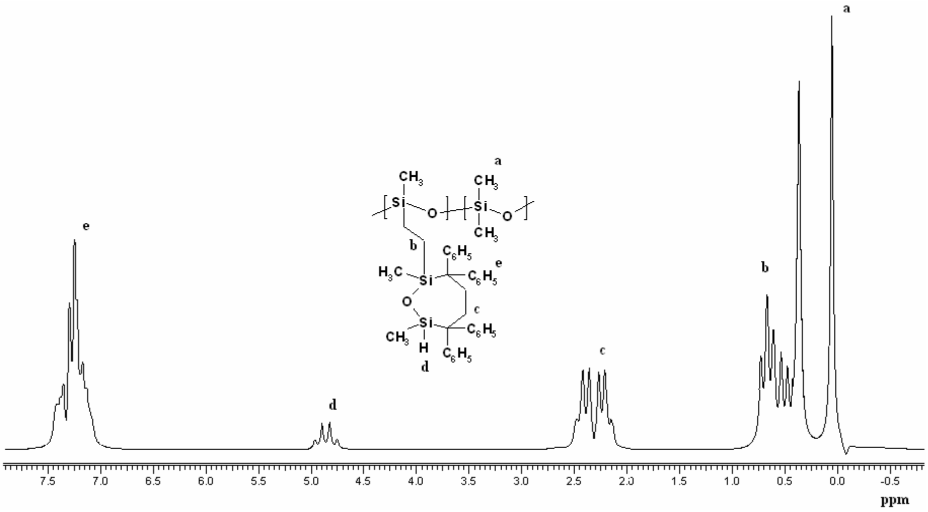


Figure 1. ^{1}H-NMR Spectrum of PCS_{1-4}

FTIR (λ, cm^{-1}): 3000, -CH- (arom.); 2930, -CH-(alkyl); 2150, -Si-H; 1585, C-C; 1480, C-C; 1425, Si-C_6H_5; 1250, Si-CH_3; 1025, Si-O-;780, Si-CH_3; 730, Si-C_6H_5; 690, C-H.

Synthesis of the carbosiloxane network (CS-P_{1-4})(Fig.2)

TBAH (0.5% mol/ precursor) was added to 1.5 g of polysiloxane precursor, stirred for approx. 1 min., and then allowed to stand until it gelled (approx. 55 min. at room temperature depending on the precursor structure). The resulted material was investigated by IR, DSC and TGA.

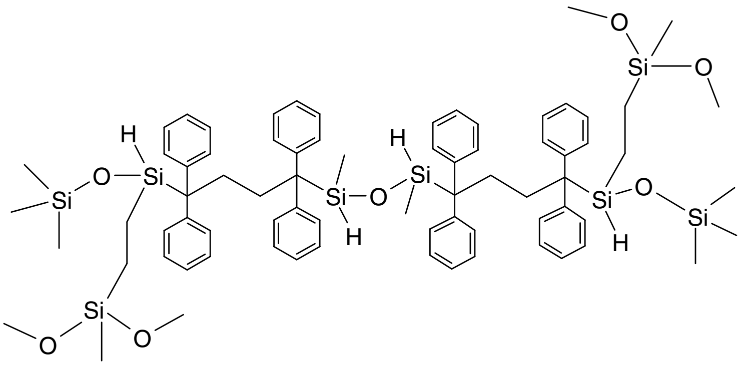


Figure 2. Crosslinking of PCS_{1-4}

The IR spectrum shows similar absorption bands for all the products:

FTIR (λ, cm^{-1}) : 2998, -CH- (arom.); 2950, -CH-(alkyl); 2150, -Si-H; 1470, C-C; 1415, Si-C_6H_5; 1250, Si-CH_3; 1020, Si-O-;840, Si-CH_3; 784, Si-C_6H_5; 590, C-H.

TGA analysis was performed in different moments of the ring-opening process. In the earlier stages, the TGA profile shows two distinct weight loss transitions for all the polymers with maximum decomposition peaks at 320°C and 510°C. During the reaction the TGA changed gradually toward a profile with a single weight loss transition and a maximum at 540°C.

DSC analysis of the solid material shows negative Tg values as presented in Table 1.

TABLE 1. Effect of precursor structure on the glass transition temperature

Precursor	Linear polysiloxane, Mw, g.mol^{-1}	Cycles content, %	CS-P$_{1-4}$ Tg, °C
PCS$_1$	2600	11.06	- 73.5
PCS$_2$	5200	12.01	- 63.3
PCS$_3$	2300	18.02	-110.2
PCS$_4$	4800	21.04	-103.7

No change in volume was observed after polymerization and the material showed no measurable evidence of shrinkage. All the resulted cross-linked polymers are glassy materials.

It is rather difficult to obtain information concerning the reaction progress and the formation of the polymeric network because the system crosses over multiple inhomogeneous states where both liquid and solid phases coexist. A method of approach is to take into account only parts of the reacting domains where the properties are similar to those corresponding to the homogeneous systems. Therefore it is possible to define the pre-gelation as a state where the viscosity of the liquid precursor increases rapidly at constant rate in the absence of a solid polymeric matrix. The existence of this specific crosslinking stage is determined by the mobility of the reactive species during the diffusion processes in both liquid and solid polymeric phases. Its duration could be obtained graphically by plotting the viscosity of the reaction mixture versus time [23].

A study of the crosslinking reaction evolution within the pre-gelation state was made by monitoring of the ring-opening process.

The experiments were done in a synthesis setup built using several 25 cm^3 reaction flasks attached to the same reflux condenser. Each reactor was charged with 5 g of polycyclic precursor and brought to the prescribed temperature. Then, the catalyst, 0.2% mol, was added under dry nitrogen atmosphere. One by one, at measured time intervals each reactor was detached from the system. The content was solved in cold toluene, washed until neutral pH, dried over magnesium sulphate, then ultracentrifugated to separate the solids. The final stage was a vacuum distillation to eliminate the solvent. Small amounts from the resulted liquid product were used for inherent viscosity measurements as 2% solution in toluene (Fig. 3).

The remaining part was analyzed by ^{1}H-NMR in order to establish the amount of the transformed cyclic structure. This was made by comparing the integrated signals at 4.85 ppm and 4.15 ppm assigned to the Si-H proton of the cyclic and ring-opened carbosiloxane respectively. The experimental results representing the cyclic fragments consumptions during the reaction are presented in Fig. 4.

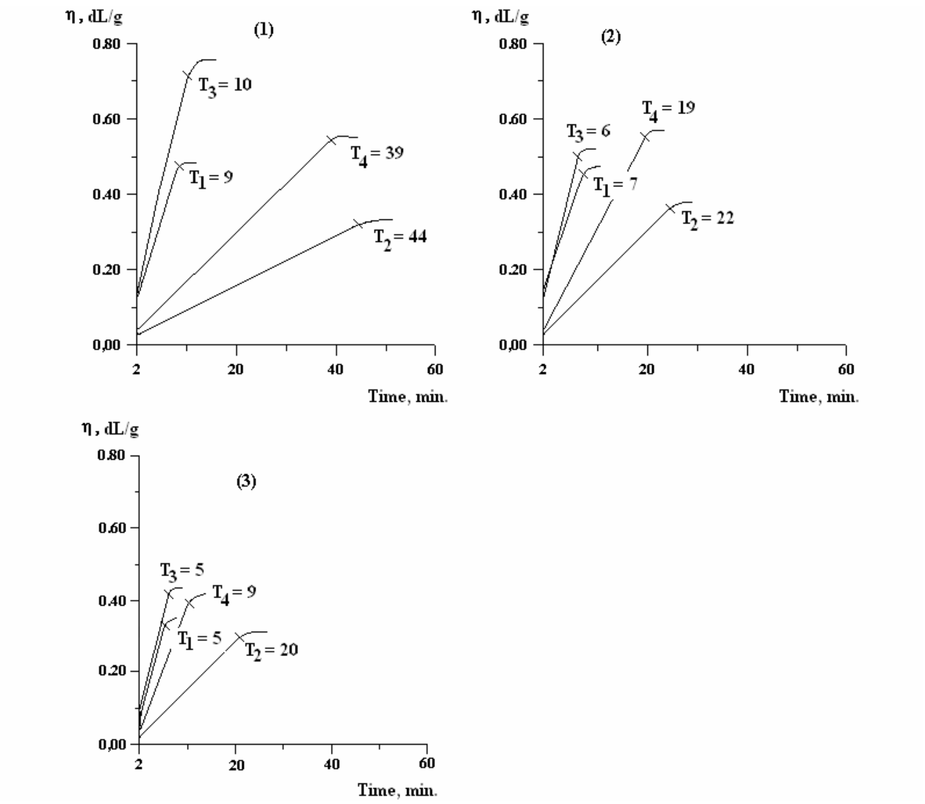


Figure 3. Inherent viscosity versus time during crosslinking of PCS_{1-4} at: (1) 25°C ; (2) 50°C; (3) 80°C. T_{1-4} : upper limit of time for the pre-gelation state corresponding to polymers PCS_{1-4}. Total gelation time (TGA)= 56 min.(25 °); 52 min. (50°C); 45 min. (80°C)

Results and Discussions

This work provides a strategy for the preparation of hybrid organic-inorganic cross-linked networks by ring-opening polymerization of a cyclo-linear polydimethylvinylsiloxane liquid precursor. Ring strain provides the thermodynamic driving force, the chain growth mechanism eliminates co-reactants, solvents, and condensation products, and the ring-opened structure compensates for the volumetric losses and shrinkage resulted from the polymerization.

The polycyclocarbosiloxane precursor synthesis method ensures control over the thermo-mechanical properties of the network by varying of the dimension and the chemical structure of both polydimethylvinylsiloxane chain and cyclocarbosiloxane segment.

Spectral analyses of the polydimethylcyclocarbosiloxane precursor were performed in order to investigate the chemical structure [22].

The ^{1}H-NMR spectrum (Fig.1) shows the characteristic chemical shifts corresponding to the ethylene bridge formation at 0.6 ppm and no evidence of the double bond protons at 6.0 ppm. On the other side, a peak visible at 4.85 ppm indicates the presence of the unreacted Si-H groups.

The IR absorption spectrum displays similar information. Thus, the –Si-H bond absorption band appears at 2150 cm^{-1} but there is no absorption band at 1600 cm^{-1} specific for the double bond. Therefore, it was assumed that the addition reaction proceeds with the formation of a polysiloxane structure with pendent cyclocarbosiloxane side groups. This excludes the intermolecular bridging and confirms earlier experiments showing that the cyclocarbosiloxane Si-H reactivity depends strongly on the reaction temperature [24].

The reaction takes place with the complete consumption of the cyclic fragments and the formation of a highly cross-linked polymer with a single thermal decomposition stage. In the earlier steps, the anionic catalyst action leads to the formation of silyl anions and attack on the carbosiloxane ring. Then, through ring-opening, the reaction system develops hyperbranching and crosslinking which finally yields the polymeric network. The evolution of the process could be observed by the TGA analysis. In earlier stages, when most of the cyclo-linear structure is present together with the cross-linked polymer, two distinct thermal decomposition stages could be observed. The lowest, at 320°C, corresponds to the untransformed cyclo-linear polymer. When the system reached the highest degree of transformation the cross-linked material exhibits only a single decomposition stage with a maximum at 540°C. In this case all the cyclocarbosiloxane segments were ring-opened structures assembled in the polymeric network.

The polysiloxane cyclo-linear architecture offers the important advantage of control over the material thermo-mechanical properties. This control is achieved through both the chain dimension of the siloxane oligomer which affects the Tg's values of the material and the cyclic content which ensures a structural tuning within the same polymer class. It was observed that the cyclocarbosiloxane content has a stronger influence on the Tg values than the polysiloxane chain dimension (Table 1).

A study of the pre-gelation state during ring-opening reaction of polycyclocarbosiloxanes with various molecular weights and cyclic content was done. For this purpose, samples of liquid precursor were allowed to react at various temperatures to observe the viscosity and ^{1}H-NMR spectrum modification. Using the graphical plot of the inherent viscosities versus time it was possible to establish the limits of the pre-gelation state and the domain of linear variation of viscosity. Within this region, the crosslinking reaction occurs mostly in the liquid state and allows all functional groups to react until gelation is reached. This means that at this point the reactive groups have a greater mobility and a moderate diffusion constraint. Subsequently, the increase of the viscosity takes an exponential course with the formation of the solid lattice and "trapped" oligomers with low mobility. The increase in temperature has a relaxing effect on the rigidity of this lattice and leads to the decrease of the overall reaction time.

It was noticed that within the first 2 min. of reaction, a sudden variation of viscosity takes place in all cases. Then, the reaction evolves according to the chemical structure of the material. Therefore, bellow 80°C the viscosity of polymers PCS_1 and PCS_3 increases faster compared with PCS_2 and PCS_4. Above this temperature the differences become smaller excepting PCS_4 which shows in both cases a slow variation of viscosity. By analogy with the anionic polymerization of the cyclosiloxanes in similar conditions, this behavior was assigned to the aggregation of the reactive species present in the system [25].

A graphical evaluation of the kinetic parameters was done by processing the experimental results during the ring-opening reactions for PCS_{1-4} (Fig. 4).

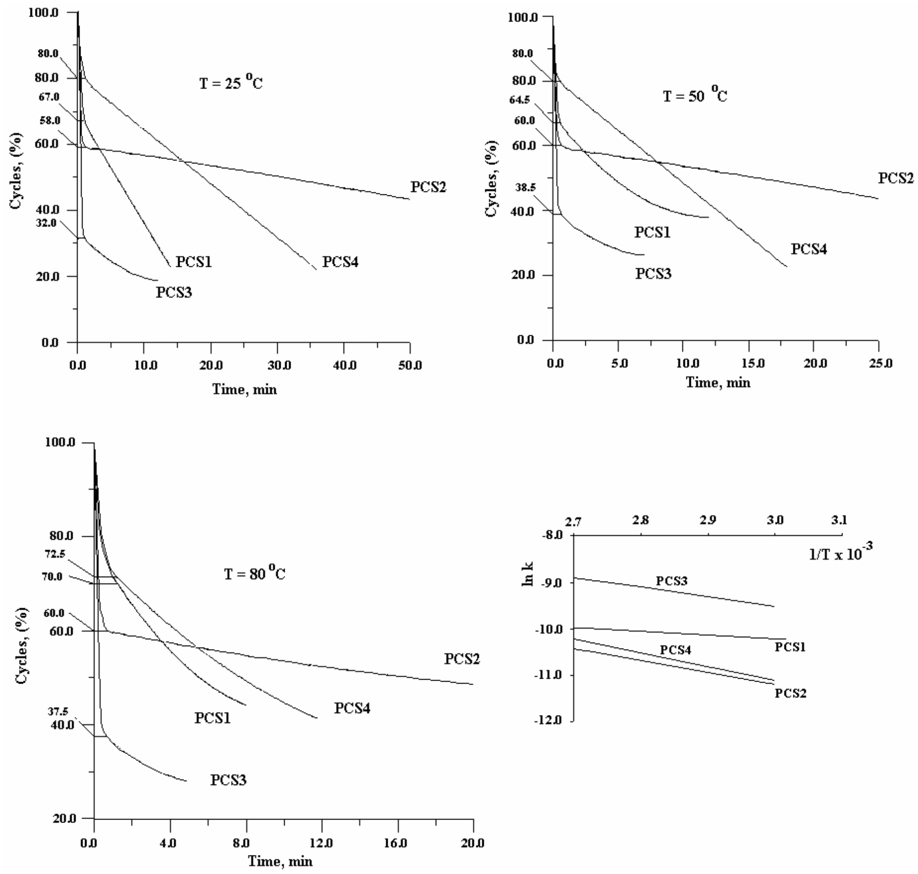


Figure 4. Graphical evaluation of the kinetic parameters

These representations show two reacting domains: the first one exhibits a rapid decrease of the cyclic fragment concentration and corresponds to the initiation stage of the reaction with the formation of small branched structures; the second one shows a slow variation of the reactant concentration and was assigned to propagation and equilibration reactions. This stage was taken into account for the calculation of the reaction ratios constants and activation energies.

Because of the similarity with the ring-opening reaction mechanism of cyclosiloxane the reaction ratios constants were calculated using a first order kinetic (Table 2) [26].

TABLE 2. Reaction ratio constants at various temperatures

Precursor	Temperature, °C			Ea, kJ/mole	A s^{-1}
	25 k x 10^{-4}, s^{-1}	50 k x 10^{-4}, s^{-1}	80 k x 10^{-4}, s^{-1}		
PCS_1	0.36	0.44	0.46	6.93	$4.4*10^{-4}$
PCS_2	0.13	0.25	0.28	21.60	$3.3*10^{-2}$
PCS_3	0.77	1.06	1.41	16.62	$5.5*10^{-4}$
PCS_4	0.14	0.27	0.35	25.76	0.15

Knowing the reaction ratio constants makes possible the calculation of the activation energy using the classical Arrhenius equation, followed by the graphical representation of ln k versus 1/T (Table3). These results show that besides the cyclocarbosiloxane structure, the molecular weight of the precursor has a strong influence over the reactivity. Therefore, this relation could be useful to design encapsulating precursors with gelation times corresponding to various technical requirements. For the polysiloxane structures presented in this study, the lower molecular weights precursors ensure shorter gelation time.

Conclusion

Precursors for cross-linked polymeric materials were synthesized via addition of polydimethyl-co-methylvinylsiloxane to 2,7-dimethyl-2,7-dihydro-3,3,6,6-tetraphenyl-1-oxa-2,7-disilacycloheptane.

Through anionic ring-opening reaction these precursors were transformed in transparent glassy materials useful for encapsulation or coatings. The novel cyclo-linear architecture ensures control over the thermo-mechanical properties of the material.

References

1 Schmidt H (1994) Journal of non-crystalline solids 178:302; Sugahara Y (1999) Journal of the Japan Society of Colour Material 72:373; Yamamoto K, Sakata Y, Nohara Y, Takahashi Y, Tatsumi T (2003) Science 300:470
2 Shea KJ, Loy DA, Webster OW (1989) Chem Mater 1:572; Rahimian K, Loy DA, Wheeler DR (2002) Macromolecules 35(7):2452
3 Bourget L, Corriu RJP, Leclercq D, Mutin PH, Vioux A (1998) J Non-Cryst Solids 242:81; Hay JN, Raval HM (2001) Chem Mater 13(10): 3396
4 Hay JN, Raval HM (1998) J Mater Chem 8:1233
5 Kaddami H, Gerard JF, Pascault JP (1999) Mater Res Soc Symp Proc 576:51
6 Ellsworth MW, Novak BM (1991) J Am Chem Soc 113:2756
7 Novak BM, Davies C (1991) Macromolecules 24:5481
8 Ellsworth MW, Novak BM (1992) Polym Prepr (Am Chem Soc div Polym Chem) 33:1088
9 Ellsworth MW, Novak BM (1993) Chem. Mater 5:839
10 Novak BM (1993) Adv Mater (Weinheim, Germany) 5:422
11 Novak BM, Ellsworth MW (1993) Mater Sci Eng A162:257
12 Wei Y, Jin D, Yang C, Wei G (1996) J Sol-Gel Sci Technol 7:191
13 Wei Y, Jin D, Yang C, Wei G (1996) Polym Mater Sci Eng 74:244; Myles AJ, Zhang Z, Liu G, Branda NR (2000) Org Lett 2(18): 2749
14 Nuyken O, Boehner R, Erdmann C (1996) Macromol Symp 107:125
15 Verstegen EJK, Faasen JHP, Stapert HR, Duineveld PC, Kloosterboer JG (2003) J Appl Polym Sci 90:2364
16 Klee JE, Walz U, Hoelter D, Frey H, Muelhaupt R (1998) Angew Makromol Chem 260:71
17 Rokicki G (2000) Prog Polym Sci 25:259
18 Cazacu M, Marcu M (1993) Rom Pat 93-00827
19 Luchian N, Sacarescu L, Rugina T, Harabagiu V, Cotzur C (1991) Polymer Bulletin 26:1; Luchian N, Sacarescu L, Marcu M (1995) Revue Roumaine de Chimie 40:3; Sacarescu L, Luchian N, Marcu M (1995) Revue Roumaine de Chimie 40:5
20 Cazacu M, Marcu M (1995) Macromol. Rep. A32:1019
21 Speier JL, Webster JA, Barnes GH (1957) J Am Chem Soc 79:974

22 Smith AL (1991) Analysis of Silicones, J. Wiley & Sons, New York

23 Sacarescu L, Capmare E, Ardeleanu R, Sacarescu G (2002) Eur Polym J 38:983

24 Sacarescu G, Sacarescu L, Ardeleanu R, Marcu M, Voiculescu N (2000) Eur Polym J 36: 2089

25 Mazurek M, Scibiorec M, Chojnowski J, Zavin BG, Zhdanov AA (1980) Eur Polym J 16: 57

26 Andrianov KA, Yakushkina SE (1962) Izv Akad Nauk SSSR Ser Khim 1396