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PREPARATION AND INVESTIGATION OF MODIFIED IMIDE-SILOXANE COPOLYMERS[1]

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Abstract

A study has been carried out on the preparation of some modified imide-siloxane copolymers. This has been accomplished by means of addition of α,ω–dihydropolydimethylsiloxanes to N,N'-dialkenyldiimides by hydrosilylation reaction. The copolymers were characterized by IR and NMR spectroscopy. The molecular mass, molecular mass distribution, thermal properties and chemical resistance of the copolymers were determined.

Keywords: poly-(imide-siloxane), segmented copolymers, poly-(dimethylsiloxane), polyimides.

1. Introduction

Silicone-containing polyimides [1, 2] have been investigated in order to improve the processibility, thermo-oxidative stability and mechanical properties by incorporation of silicon into the polymer chain.

A new group of polymers called polysiloxane-imides (PSI) is obtained by polycondensation of aromatic dianhydrides with organic diamines and aminofunctional capped di- and/or polysiloxanes [3–6]. The aim of the present work is to reveal another method for preparing novel imide-siloxane copolymers.

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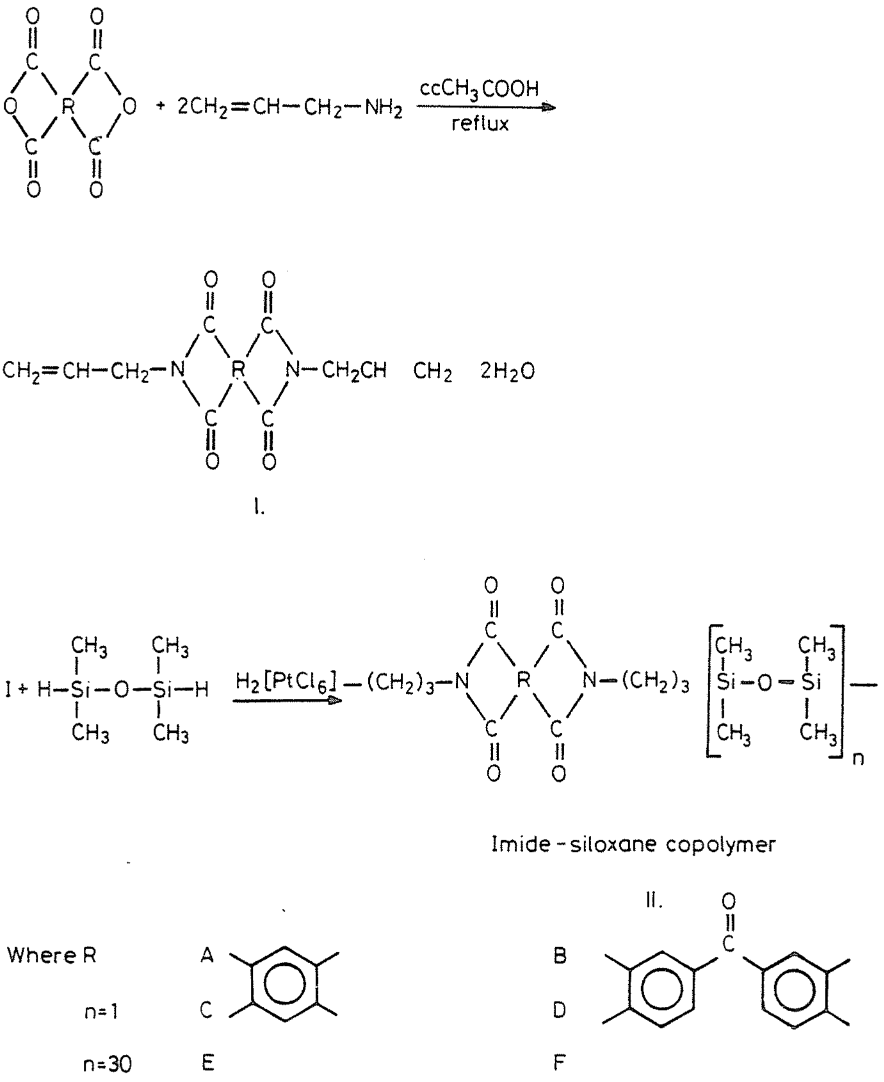
[1] This work was supported by the OTKA 641.

2. Experimental

The synthesis of these copolymers was carried out according to the following reaction scheme:



In the first reaction two types of (I) were prepared: N,N'-diallylpyromellitdiimide (referred to as IA component), and N,N'-3,3',4,4'-benzophenontetracarboxylicdiimide (referred to as IB component).

The synthesis of these compounds has been reported earlier [7]. In this work a new route was used to prepare these compounds, similar to those used before for N-allylphthalimide [8].

Preparation of N,N'-diallylpyromellitdiimide (IA)

In a three-necked flask fitted with a mercury sealed mechanic stirrer, dropping funnel and reflux condenser (ending in a $CaCl_2$ tube) 21.6 g (0.01 mole) of pyromellitic dianhydride in 180 cm^3 acetic acid solution was placed. Cooling the flask with ice bath 11.4 g (0.2 mole) allylamine was added dropwise with continuous stirring in one hour. After the addition, the ice bath was removed and the reaction mixture was refluxed for one and a half hours. The content of the flask was poured into 170 cm^3 distilled water, the mixture was brought to the boil and then cooled, the product was filtered and washed several times with water, then with methanol. The powdered product recrystallized from chloroform gave 25 g (0.085 mole) of N,N'-diallylpyromellitdiimide in form of glistening white plates. The yield was 85%.

Preparation of N,N'–diallyl–3,3'–4,4'-benzophenontetracarboxylicdiimide (IB)

IB was prepared, in the same steps as mentioned above. It was obtained as a yellow powder with a yield of 75%.

Melting points and molecular masses for monomers (IA) and (IB) are shown in *Table 1.*

Table 1
Melting points and molecular masses for the monomers prepared

Monomer	Mol.mass calcd.	Mol. mass found	Melting points °C		
		(1)	(2)	(3)	(4)
IA	296	292	232-234	230	225
IB	400	390	154-156	155	150

(1) By boiling point elevation using chloroform as solvent
(2) By microscopic apparatus
(3) By DSC, heating rate 10 °C/min
(4) By DTA, heating rate 5 °C/min

Preparation of Imide-siloxane Copolymers [of IA, IB and 1,1,3,3-tetramethyl-disiloxane]

Addition in a molar ratio of 1:1 [of IA and 1,1,3,3-tetramethyl-disiloxane] (IIC).

The addition reaction was carried out with equimolar ratios between the reactants.

The reaction was carried out in a dry clean three-necked flask equipped with condenser, dropping funnel and $CaCl_2$ tube.

7.2 g (24 mmole) of N,N'-diallylpyromellitdiimide was dissolved in 70 cm^3 of dry benzene at 80 °c, 55 μl 0.5 wt% hexachloroplatinic acid solution in ethyleneglycoldimethyl-ether was used as catalyst and 3.25 g (24 mmole) of 1,1',3,3'-tetramethyldisiloxane was added dropwise to the above reaction mixture in one hour. The reaction mixture was heated further for 2h at 110 °C. Following the distillation of the solvent from the reaction mixture under vacuum, the product was recrystallized from acetone/ethanol mixture (in 50/50 ratio), to give 8 g (0.018 mmole) product, yield: 87% imide-siloxane copolymer, in the form of a white powder. Mp. measured by microscopic apparatus: 187-190 °C.

The same procedure was used as mentioned above for preparing copolymer (IID).

Table 2

Symbols, yields, elemental analysis and melting points (1) for the copolymers prepared

Symbols	Yields %	Melting points °C	Elemental analysis %			
				C	H	N
II C	87	187-190	Calc.	55.99	5.87	6.52
			Meas.	56.74	5.54	6.93
II D	90	98-100	Calc.	60.84	5.44	5.25
			Meas.	62.48	4.73	5.74

(1) by microscopic apparatus

Preparation of imide-siloxane copolymers of [IA, IB and dihydropolydimethyl-siloxane (n = 30) oligomer]

Addition in molar ratio of 1:1 [of IA and (HSi_{30})] (IIE).

In a dry three-necked flask equipped with mercury sealed mechanical stirrer, reflux condenser, drying tube and dropping funnel 10 g (0.033 mole) of IA was dissolved in 70 cm^3 of dry benzene at 80 °C, and 55 μl of 0.5 wt% hexachloroplatinum acid solution used as catalyst and 72.79 g, 0.033 mole of HSi_{30} was added dropwise in one hour. After the addition, the mixture was heated for further 3 hours at 110 °. The solvent was distilled off in vacuum, then the mixture was cooled and 50 cm^3 of benzene was added. The reaction mixture was stirred for half an hour at room temperature, then the solvent was removed from the reaction mixture by vacuum distillation 75 g (0.029 mole, 88%) of product was yielded.

The same procedure was used as mentioned above for preparing copolymers (IIF).

Yields and viscosity data for the copolymers IIE–IIF are shown in *Table 3.*

Table 3
Symbols, yields and viscosity data for the copolymers prepared

Symbols	Yields, %	ηmPa.s (1)
IIE	88	70000
IIF	89	42570

(1) By Rheotest II rotation viscometer at 25 °C

3. Characterization of Imide-siloxane Copolymers

3.1. Infrared Spectroscopy

The IR spectra of the investigated compounds were recorded by a Specord instrument, in transmission, and using ATR. The ATR attachment with a KRS–5 crystal aligned to beam incidence angles 30°, 45° or 60°. KBr tablets were used for solids and KBr plates for liquids. The spectra reflect the structure of the respective compounds. The IR spectrum of compounds IA and IB shows absorptions at 1700–1720 cm^{-1} and at 1770–1776 cm^{-1}

assigned to the symmetric and asymmetric stretching vibrations of the imide C=O ring groups. Absorptions at 1105–1115 cm^{-1} and at 730 cm^{-1} were due to deformation vibrations of imide C=O ring groups. The spectra of benzene rings show a good agreement with that in the literature. The $\nu_{C\text{-}H}$ stretching vibration can be easily distinguished in the region 3060–3100 cm^{-1}, and the $\nu_{C\text{-}C}$ stretching vibrations at 1440 cm^{-1} and 1600–1610 cm^{-1}. For copolymers (IIC–IIF) additional bands were observed in the spectrum as follows: the symmetric $-CH_3$ deformation ($\delta_{C\text{-}H_3}$) gives a very intense band for $Si\text{–}CH_3$ in the 1255–1265 cm^{-1} region and it is the most characteristic band of $Si\text{–}CH_3$. Compounds containing Si–O–Si groups have broad absorption at 1080–1000 cm^{-1} due to the asymmetric Si–O–Si stretching, depending on the mass and the inductive effects of the other groups on the silicon. The infrared spectrum of copolymer IIC is shown in *Fig. 1.*

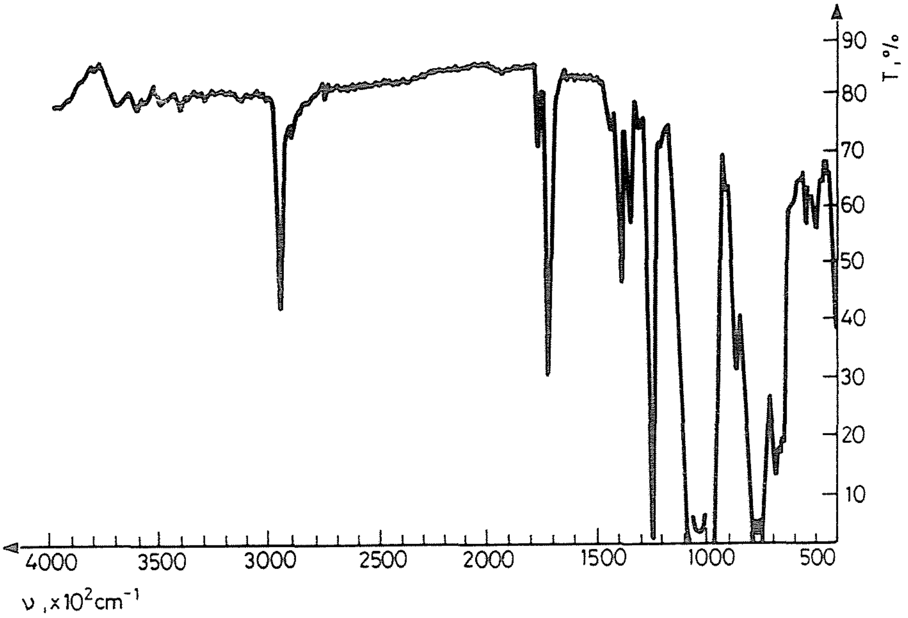
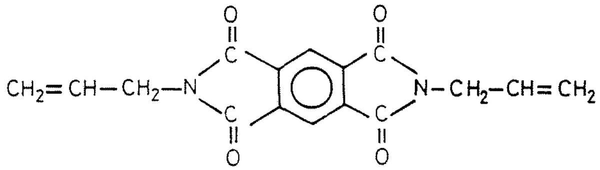


Fig. 1. Infrared spectrum of IIC copolymers

3.2. Nuclear Magnetic Resonance Spectroscopy

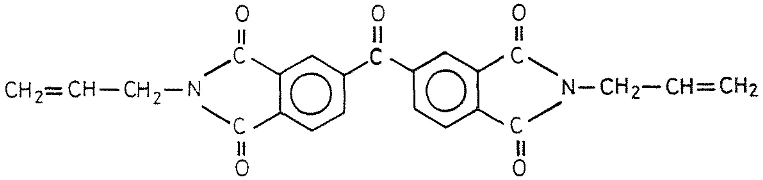
The measurements were carried out by a JEOL PX–100 type PT–NMR instrument at 100 MHz measuring frequency in $CDCl_3$ using TMS as standard. The measured chemical shifts were given in ppm units on scale $\delta_{TMS} = 0$. The aim of the ^{1}H–NMR investigations was to prove the assumed structures of the synthesized (IA–IB) compounds. The assignment of ^{1}H–NMR measurements will be presented in the following, where *s* = singlet, *m* = multiplet, *d* = dublet, *t* = triplet, *q* = quartet.

Compound IA



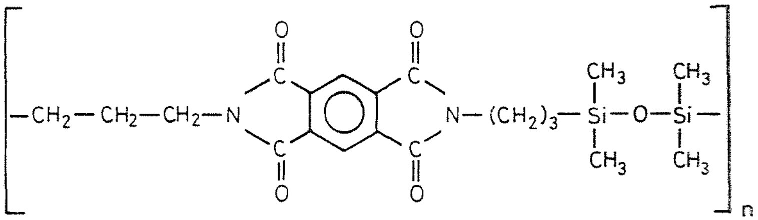
δ 4.36 ppm (4H, d, 2x$N–CH_2$), 5.18–5.28 ppm (4H, m, 2x$CH=CH_2$–), 5.66–5.88 ppm (2H, m, 2x$CH=$), 8.30 ppm (2H, s, aromatic)

Compound IB



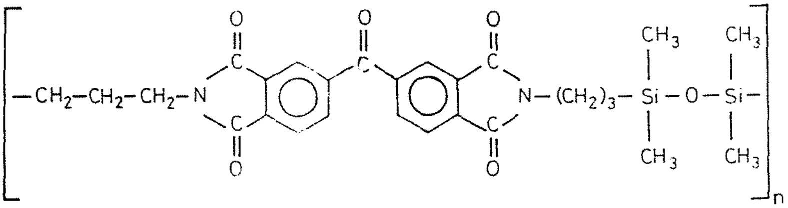
δ 4.36 ppm (4H, d, 2x$N–CH_2$), 5.18–5.28 ppm (4H, m, 2x$CH=CH_2$–), 5.66–5.90 ppm (2H, m, 2x$CH=$) 8.02–8.16 ppm (6H, s, aromatic)

Compound II C



δ 0.03 ppm (s, $Si–CH_3$, 12H), 0.40–0.7 ppm (m, $Si–CH_2$–, 2H), 1.5–2.0 ppm (m, $CH_2–CH_2–CH_2$–, 2H), 3.53–3.82 ppm (t, $N–CH_2–CH_2$, 2H), 4.29 ppm (m, $N–CH_2–CH$, 2H), 5.16–5.34 ppm (t, $CH_2=$, 2H), 5.7–5.9 ppm (q, $CH_2=CH–CH_2N$, 1H), 8.2 ppm (s, 2H, aromatic)

Compound IID



δ 0.42 ppm (s, Si–CH_3, 12H), 0.4–0.64 ppm (m, Si–CH_2–, 2H), 1.62–1.68 ppm (m, SiCH_2–CH_2–, 2H), 3.62–3.76 ppm (t, NCH_2–, 2H), 4.2–4.4 ppm (d, N–CH_2–, 2H), 5.12–5.4 ppm (t, N–CH_2=, 2H), 5.72–6.0 ppm (m, CH=, 1H), 7.996–8.2 ppm (m, aromatic, 6H)

As an example the nuclear magnetic resonance spectrum for IIC copolymer is shown in *Fig. 2*.

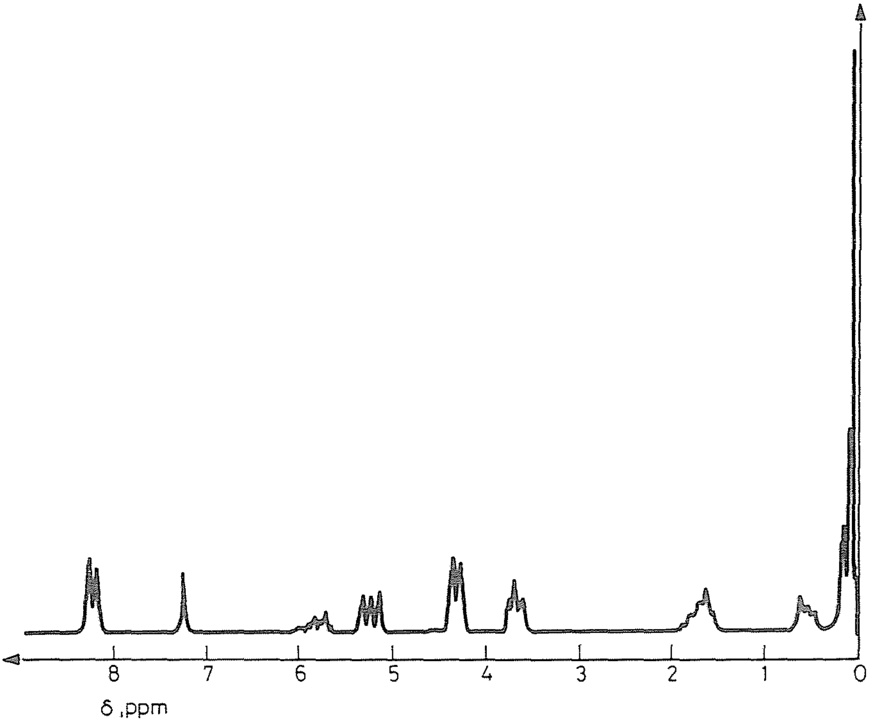


Fig. 2. NMR proton spectrum of IIC copolymers

Table 4
Molecular mass determination for the polymers prepared

Sample	M_n (1)	M_w (1)	M_w/M_n (1)	M_n (2)	M_n (3)
IIC	662	1388	2.10	669	700
IID	611	911	1.49	674	668

(1) By GPC method
(2) By VPO method
(3) By boiling point elevation method using CCl_4 as solvent

3.3. Molecular Mass Determination

The average molecular mass was determined at 60 °C by Vapour Pressure Osmometric (VPO) method using the known calibration substance Squalan and toluene as solvent. The molecular mass was also measured by boiling point elevation method using CCl_4 as solvent. Molecular mass distribution was determined by gel permeation chromatography (GPC).

The GPC measurements were performed on a Waters ALC/GPC–201 instrument equipped with differential refractometer and absorption UV detector, using a series of 5 U-Styragel columns ($10^5 + 10^4 + 10^3 + 100 +$ 50 nm pore size). THF was used as the mobile phase at a flow rate of 1.5 ml/min at room temperature. This column series was characterized by calibration with polystyrene standards. The molecular mass distribution for copolymers IIC–IID was determined by GPC calibration using polystyrene as standard, the calibration method was described in an earlier publication [9]. Average molecular mass values, and the molecular mass distribution are shown in *Table 4*.

Molecular mass and intrinsic viscosity values for copolymers IIE–IIF are shown in *Table 5*.

Table 5
Molecular mass and intrinsic viscosity values for the polymers prepared

Sample	$[\eta]$ dl/g (1)	M_n (2)	M_w (2)	M_w/M_n (2)	M_n (3)	M_n (4)
Si_{30}-H	-	2196	2858	1.3	1690	1800
IIE	0.29	12883	50135	3.89	15645	10830
IIF	0.18	8213	27225	3.31	12516	8970

(1) The intrinsic viscosity was determined
by a Cannon-Ubbelohde viscosimeter in toluene as solvent at 25 °C
(2) By GPC method
(3) By VPO method
(4) By boiling-point elevation method using CCl_4 as solvent

3.4. Thermal Analysis

A DuPont 1090 DSC instrument and a Derivatograph MOM 3427 type DTA apparatus was used to determine the melting points (T_m) and the glass transition temperature (T_g) of the monomer with programmed heating rate of 10 °/min and cooling rate of 20 °C/min to determine melting points, while a heating rate of 20 °C/min was used to determine the glass transition temperature.

Thermogravimetric analysis (TG) was performed on a DuPont 951 instrument. Scans were run at 10 °C/min in argon atmosphere.

The glass transition temperatures and melting point values for the polymers prepared are listed in *Table 6*.

Table 6

Glass transition temperatures and melting points data for the polymers prepared

Copolymer Mol. ratio	Tg (1) °C	Endotherm onset, °C	Endothermic peak, °C	Tm (1) °C	Tm (2) °C
IIC	20–35	162	176	180	165
IID	32–42	90	93	100	95

(1) By DSC
(2) By DTA

The thermogravimetric measurements were carried out in argon and air atmosphere. The data corresponding to 5 and 10% weight loss, respectively, for the copolymers prepared are shown in *Table 7*.

Table 7

Thermogravimetric analysis data for the polymers prepared

Sample	Thermal stability in argon			Thermal stability in air		
	T_0°C	T_5°C	T_{10}°C	T_0°C	T_5°C	T_{10}°C
IIC	210	240	265	190	215	235
IID	255	313	338	235	290	300
IIE	375	410	440	300	365	390
IIF	400	445	470	328	395	425

T_0, initial decomposition temperature
T_5 5% mass loss temperature
T_{10}, 10% mass loss temperature

All copolymers exhibit good high temperature stability. The thermal stability increases with increasing molecular mass as shown with copolymers IIE and IIF, respectively.

3.5. *Chemical Resistance*

The solubility behaviour of imide-siloxane copolymers in different solvents with known solubility parameters has been examined, the solubility parameters for different solvents were obtained according to [10]. For prediction of the solubility parameter the following equation was used [11]:

$$\delta = (E_{\mathrm{coh}}/V)^{1/2},$$

where E_{coh} was the cohesive energy and V was the molecular volume.

The best solvent of a given polymer is the liquid whose cohesive energy density (CED) is similar to that of polymer. This consideration is the basis of the method of determining the CED of a polymer.

Solubility values for the imide-siloxane copolymer series were measured using 100 mg polymer in 5 ml of different solvents. The solubility of imide-siloxane copolymers in different solvents is shown in *Table 8.*

Table 8
Solubility properties for the copolymers prepared

Solvent	Solubility parameters $(\mathrm{J/cm^3})^{0.5}$	IIC	IID	IIE	IIF
DMF	24.58	+	++	m	m
Methanol	29.70	–	–	–	–
Ethanol	25.80	–	–	–	–
$CHCl_3$	18.90	++	++	++	++
CH_2Cl_2	19.71	++	++	++	++
Toluene	18.08	+	++	++	++
CCl_4	17.60	+	+	++	++
Cyclohexane	17.00	–	–	++	++

++: soluble cold; +: soluble hot; – : insoluble, m: miscible

Table 8 shows that the solubilities of siloxane-polyimide copolymers are higher than those of organic copolyimide in various solvents [12]. The solubility parameter for organic polyimides is between 26.5–26.8 $(\mathrm{J/cm^3})^{0.5}$.

The solubility of imide-siloxane copolymers in various solvents may be due to the flexible Si–O–Si and the aliphatic $-CH_2-CH_2-CH_2$-linkages in the main chain. The polysiloxane fragment caused the copolyimides to be more soluble in various solvents. Such behaviour is unusual for polyimides.

Conclusion

The advantage of the hydrosilylation method is that the mentioned imide-siloxane copolymers can be prepared in an easier and cheaper way and without abnormal reactions, than by the methods reported in literature.

Our results are highly promising specially for mixing these copolymers with other silicone polymers for high temperature vulcanizing (HTV) process. The results of work in this field will be published later.

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