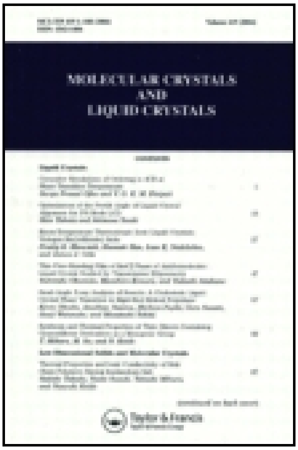

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Siloxane and N-Acetyliminoethylene Based Copolymers Obtained by Combined Polymer Synthesis Techniques

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Siloxane and N-Acetyliminoethylene Based Copolymers Obtained by Combined Polymer Synthesis Techniques

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The paper discusses different synthetic approaches yielding block and graft copolymers containing siloxane and/or N-acetyliminoethylene moieties. Since the corresponding homopolymer sequences are obtained by quite specific mechanisms, combined techniques are required to build different types of copolymers.

Keywords: siloxane; N-acetyliminoethylene; block and graft copolymers

INTRODUCTION

Siloxane and N-acetyliminoethylene containing block and graft copolymers are quite peculiar polymeric materials from the point of view of their synthetic approaches and properties. Both classes of copolymers are practically obtained only by combined techniques and each of them possess unique characteristics.

Siloxane copolymers are hybrid materials whose components are obtained by quite different synthetic approaches. Siloxane sequences can be prepared mainly by hydrolysis of silicofunctional organosilanes or by ionic polymerization of cyclosiloxanes, while the organic segments are reachable by the well known chain or step growth polymerization mechanisms. In fact, siloxane containing copolymers were prepared by the one-step method only by successive living anionic copolymerization of unsaturated monomers and cyclosiloxanes[1]. All other techniques associate two or more reaction mechanisms (one specific to the organic sequence, the other yielding the siloxane segment)[2].

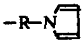
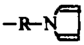
2-substituted-2-oxazolines (ROZOs) have been extensively investigated in the last years since their cationic ring-opening polymerization, having a *living* character under appropriate reaction conditions, is a convenient method to prepare poly(N-acyliminoethylene) (PROZO) based polymer materials[3-6]. The unique properties of PROZOs, such as high hydrophilicity and miscibility with organic polymers, give rise to various applications - as non-ionic polymer surfactants, functional hydrogels, stabilizers for preparation of monodisperse particles, compatibilizers, adhesives. In most cases such novel polymeric materials imply the combination of PROZO with polymers derived from monomers polymerizable by other mechanisms. The obtention of such block and graft copolymers requests combined polymer synthesis techniques.

Hydrophobic, chemically resistant siloxane polymers and hydrophilic, double helix structured poly(N-acetyliminoethylene) have as common property their biocompatibility. Apart their uses as high performance materials in space industry, electronics, etc., siloxane and N-acetyliminoethylene based copolymers are suitable for biomedical applications (controlled drug delivery systems, membranes, artificial organs, contact lenses, etc.) The aim of the present paper is to illustrate different approaches yielding siloxane and/or N-acetyliminoethylene block and graft copolymers.

SILOXANE CONTAINING BLOCK AND GRAFT COPOLYMERS

Usually, organofunctional polysiloxanes are preferred as starting compounds in the preparation of block and graft copolymers containing siloxane and organic sequences linked together through hydrolytically stable Si-C units[7]. Table I presents the organofunctional polysiloxanes used in our studies as active precursors in the synthesis of copolymers.

TABLE I Organofunctional polysiloxanes used as starting compounds in the synthesis of block and graft copolymers

Code	Functional group (-R-X)*	Molecular weight range	SiMe$_2$/SiMe(RX) (molar ratio)	Ref.
PDMS-OH	e -C_3H_6-OH	1000 - 10000	-	[8,9]
PDMS-Cl	e -C_2H_4-Ph-CH_2-Cl	500 - 8000	-	[10]
	c -C_2H_4-Ph-CH_2-Cl	700 - 8000	2 - 9	
PDMS-Py	e  R: -CH_2-CH(OH)-CH_2-NH-$(CH_2)_3$-	1000	-	[11]
	c  R: -CH_2-CH(OH)-CH_2-NH-Ph-C_2H_4-	3000 - 8000	6 - 10	-

* e and c indicate end and chain functionalized samples, respectively

Siloxane-Vinyl Block and Graft Copolymers

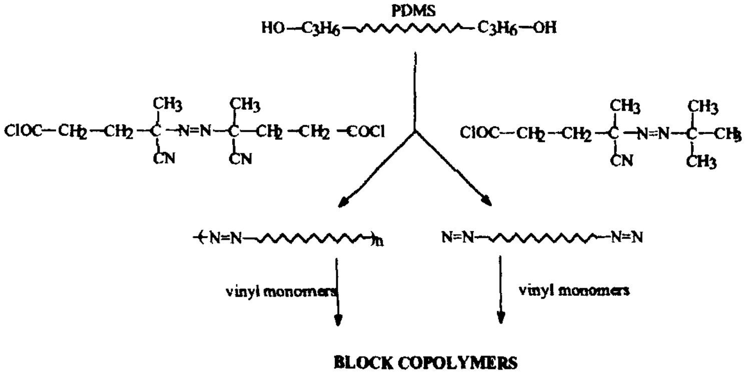
Siloxane-vinyl block and graft copolymers were obtained by three different approaches: (a) radical polymerization of vinyl monomers initiated by siloxane macroazoinitiators, (b) cationic polymerization of styrene in the presence of chlorofunctional polydimethylsiloxanes (PDMS-Cl)/$SnCl_4$ system, and (c) coupling reactions of appropriate siloxane and organic functional precursors.

Siloxane macroazoinitiator technique

The synthesis of siloxane-vinyl block copolymers via free-radical polymerization mechanism implies the use of siloxane macroinitiators.

Different types of photo- or thermally labile groups (bissilyl pinacolate[12], azo-amide[13], thiuram disulfide[14] or ditiocarbamate[15]) were introduced into siloxane chains by appropriate methods and the behaviour of the resulting products in initiating the radical polymerization of vinyl monomers was investigated. Starting from bifunctional hydroxypropyl-terminated polydimethylsiloxanes (PDMS-OH), azoester macroinitiators were obtained[8,9] by condensation with adequate azo containing organic acid chlorides (Scheme 1). Such macromolecular compounds were found to act as organic polyfunctional initiators[16], i.e., the molecular weight of the resulting copolymers increased with conversion[17]. However, they show a slightly lower efficiency as compared to the corresponding low molecular weight initiators[17].

A detailed kinetic study of the radical polymerization of vinyl monomers allowed the synthesis of hydrophobic (PDMS) - hydrophobic (polystyrene, poly(methyl, butyl (meth)acrylates), poly(vinyl acetate), etc.) or hydrophobic - hydrophilic (poly((meth)acrylic acid, poly(N-vinylpyrrolidinone)) block copolymers with predictable properties (molecular weights, sequence ratios, sequence lengths)[8,9,17].

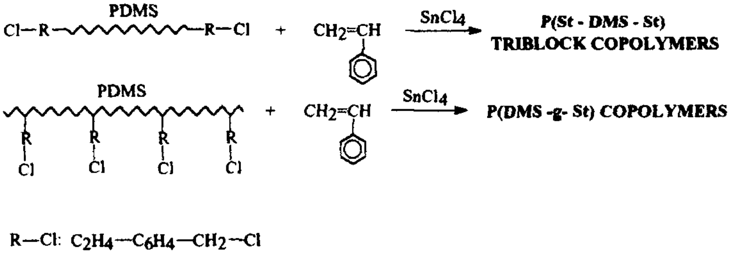


SCHEME 1 Synthesis of siloxane-vinyl block copolymers by macroazoinitiator technique.

Cationic polymerization of styrene initiated by PDMS-Cl/SnCl$_4$ system

Well defined triblock[18] and graft PDMS-polystyrene copolymers were obtained by cationic polymerization of styrene (St) in the presence of siloxane macromolecular bi- or multifunctional initiators (Scheme 2).

In low polarity solvents, the process presents a living cationic polymerization behaviour. The reaction kinetics was followed by observing the decrease of monomer characteristic peaks (δ = 5.20-5.34 and 5.66-5.86 ppm, $H_2C=$) in the ^{1}H-NMR spectrum of the reaction mixture. After 8 hours styrene was entirely consumed and the conversion increased after a second addition of the monomer. The molecular weight of the copolymers increased with the reaction time.

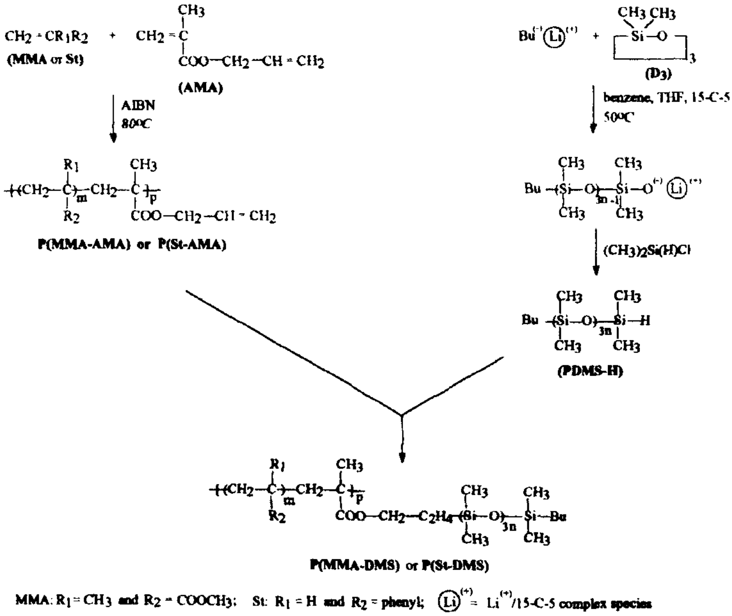


SCHEME 2 Synthesis of siloxane-styrene block and graft copolymers.

To check for any possible interactions between the cationic active species resulting from the equilibrium -PDMS-R-Cl ⇔ -PDMS-R$^{(+)}$[SnCl$_5$]$^{(-)}$ and the polysiloxane chain[19], a solution of octamethylcyclotetrasiloxane (D$_4$), benzyl chloride (BC)/SnCl$_4$ initiating system (D$_4$/BC = 50 molar ratio) and SnCl$_4$ was stirred for 24 h at 20°C. No evidence of the polymerization of D$_4$ in a carefully dried system was observed by gas chromatography and GPC: only the D$_4$ cycle was detected in the product obtained after quenching of the active species with a mixture of methanol/10% NaHCO$_3$ aqueous solution, washing the organic phase with water, drying, and evaporating the solvent (chloroform). As the siloxane bonds in D$_4$ and in linear siloxanes behave similarly to electrophilic attack[20], the pertinent conclusion is that the siloxane chain remained untouched during the cationic process.

Hydrosilation of unsaturated vinyl prepolymers with Si-H terminated siloxane oligomers

Poly(styrene or methyl methacrylate -g- dimethylsiloxane) copolymers were obtained starting from poly(styrene - allyl methacrylate) or poly(methyl methacrylate - allyl methacrylate) random copolymers prepared by the radical copolymerization of the comonomers in the presence of AIBN. These prepolymers were coupled by hydrosilation of the allyl ester side groups with monofunctional Si-H terminated PDMS in the presence of H_2PtCl_6 catalyst (Scheme 3)[21].



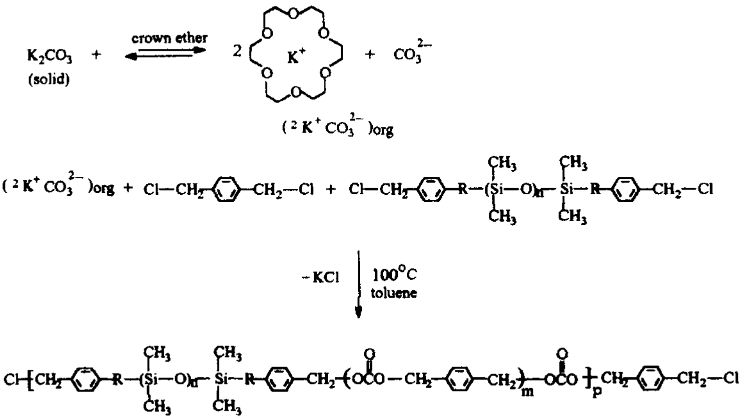
SCHEME 3 Synthesis of poly(vinyl -g- dimethylsiloxane) copolymers by hydrosilation.

Coupling of Functionalized Organic and Siloxane Precursors

Polydimethylsiloxane (A) - polyisobutene (PIB) (B) diblock copolymers were prepared by coupling of monofunctional prepolymers possessing mutual reactive groups, i.e. hydroxypropyl-terminated PDMS and succinic anhydride-terminated PIB. The BAB triblock copolymers were obtained by reacting the same monofunctional PIB with difunctional aminopropyl-terminated PDMS[22].

Siloxane-Carbonate Block Copolymers by Step Growth Polymerization

PDMS containing active chlorine end functionalities were also used as starting materials in the preparation of siloxane-carbonate copolymers through a phase transfer catalyzed process, according to Scheme 4.



SCHEME 4 Copolycondensation of p,p'-xylylene dichloride with
e PDMS-Cl.

The reaction between halogenated compounds and potassium carbonate does not occur in the absence of a phase transfer catalyst. A crown ether is able to approach a crystalline solid structure and to complex the cation. The K_2CO_3 molecules are transferred in this manner in the organic solution where they react with the chlorine functionalized compounds. Indeed, in the presence of 18-C-6 or dibenzo-18-C-6 a significant increase of the molecular weight of the siloxane prepolymer by addition of the newly formed carbonate sequence is observed. Important yields in block copolymers are attained in at least 48 h of stirring the reaction mixture at high temperature. Starting from a PDMS-Cl with Mn = 1610, the block copolymers given in Table II were obtained.

TABLE II Synthesis[*] and characterization of siloxane-carbonate block copolymers

Initial mixture[†]				Copolymer		
Siloxane/p-XCl (molar)	18-C-6/K (molar)	DB-18-C-6/K (molar)	Time (h)	Yield[††] (%)	Siloxane/carbonate[§] (molar)	Mn[#]
2.5	0.11	-	66	38.5	5.0	9000
2.0	0.10	-	50	14.6	2.5	7700
1.4	-	0.10	57	60.2	1.3	10900
0.8	-	0.10	57	33.8	1.1	9500

[*] Reaction conditions: solvent, toluene (polysiloxane conc., 20%); temperature, 100°C; K/Cl = 1.0 molar ratio

[†] p-XCl is p,p'-xylylene dichloride; DB-18-C-6 is dibenzo-18-C-6

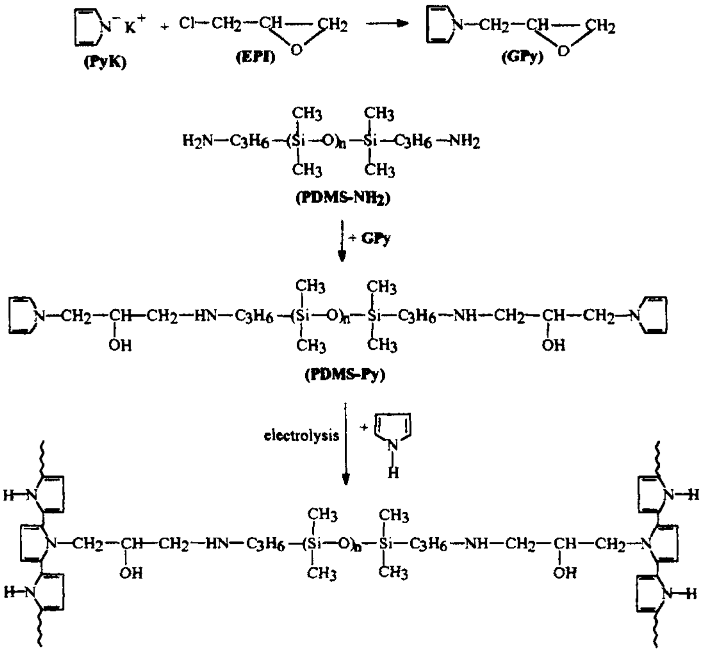
[††] After the evaporation of the solvent, the copolymer was repeatedly washed with water, hot ethanol and petroleum ether

[§] As determined from elemental analysis (Si, C, H)

[#] From chlorine content

Electrocopolymerization of Pyrrole with Pyrrolyl Functionalized PDMSs

Conducting H-type polysiloxane-polypyrrole block copolymers were synthesized by electrochemical copolymerization of pyrrole with bifunctional pyrrolyl-terminated oligosiloxanes, according to Scheme 5[11]. The resulting polymer films possess improved mechanical properties as compared to pure polypyrrole and electrical conductivities in the range of 2 - 5 S/cm for both the solution and the electrode sides of the film, indicating the homogeneity of free-standing films. Starting from chain pyrrolyl functionalized polysiloxanes, crosslinked copolymer structures are to be expected.

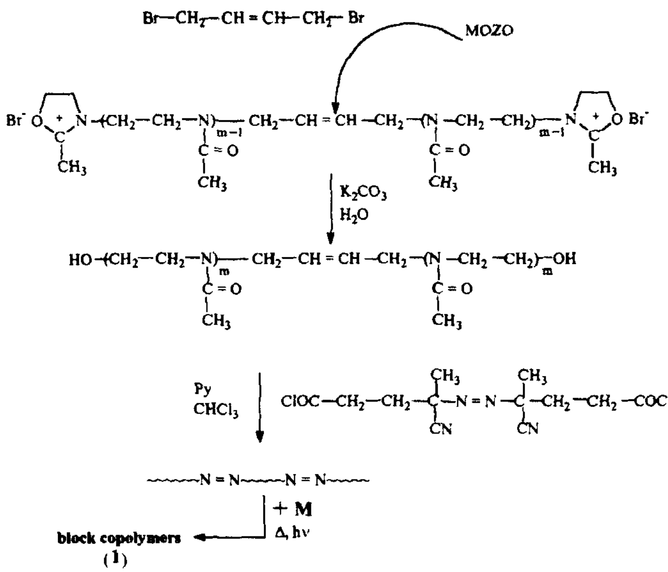


SCHEME 5 Synthesis of H-type poly(dimethylsiloxane-pyrrole) block copolymers.

N-ACYLIMINOETHYLENE POLYMERS

N-Acetyliminoethylene-Vinyl Block Copolymers by Macroazoinitiator Technique

Block copolymers containing ROZO and vinyl sequences were realized by free-radical polymerization of vinyl monomers (methacrylic acid (MA), styrene (St), methacrylic esters - methyl methacrylate (MMA), butyl methacrylate (BMA)) in the presence of poly(N-acetyliminoethylene) (PMOZO) macroinitiators[23], according to the reaction sequence given in Scheme 6.



SCHEME 6 Synthesis of MOZO-vinyl copolymers by macroinitiator technique.

The macroinitiators, prepared by coupling of hydroxyl terminated MOZO telomers with 4,4'-azobis(4-cyanopentanoyl chloride), have an initiating efficiency depending on the length of the N-acetyliminoethylene sequence. The polymerization was carried out to high conversion in solution[23] or by soapless emulsion[24] (Table III).

The neighbouring of hydrophilic (PMOZO) and hydrophobic (PSt, PMMA, PBMA) sequences yields amphiphilic block copolymers, able to act as non-ionic emulsifiers in direct or inverse emulsion systems[24]. In soapless emulsion the amphiphilic low molecular weight block copolymers formed in the early stages of the process were proved to stabilize the polymerization system[24]. By this technique the copolymer products result as micrometer sized particles with narrow size distribution and the hydrophilic PMOZO chains located on the surface.

TABLE III Polyvinyl/poly(N-acetyliminoethylene) block copolymers. Copolymerization data

Monomer	Initiator			Total conversion (%)	Polymerization procedure			
					S[*]	E		
	Code	DP of PMOZO	Mw			Dn (nm)	$\frac{Dw}{Dn}$[†]	Stability[§]
St	I_6	5.9	2030	15	+			
MA	I_6	5.9	2030	78	+			
MA	I_{20}	21.0	4640	56	+			
MMA	I_6	5.9	2030	50	+			
BMA	I_6	5.9	2030	63	+			
St[††]	I_7	6.9	2130	60		120	1.04	+
St[¶]	I_7	6.9	2130	17		197	1.21	+
St[¶]	I_{20}	21	4640	15		492	1.20	+
BMA[¶]	I_7	6.9	2130	52		424	1.50	+
MMA[¶]	I_7	6.9	2130	20		10^4-10^5	-	-
MMA+silica[#]	I_7	7.5	3500	64				+

[*] Polymerization conditions: $[M] = 2$ m; $[I_j] = 4\times10^{-2}$ m; T = 72°C; solvent, ethanol; Ar; see Ref. [23.]

[†] Dn, Dw = number and weight average diameters of the particles, respectively; Dw/Dn = polydispersity index of polymer particles

$Dn = \Sigma NiDi/\Sigma Ni$; $Dw = \Sigma NiDi^4/\Sigma NiDi^3$

[§] + stable, - unstable

[††] Reaction conditions: 0.0125g I_7/g-w; 0.05g monomer/g-w; 5h - 80°C, 1h - 90°C; Ar; see Ref. [24.]

[¶] Reaction conditions: 0.0075g I/g-w; 0.045g monomer/g-w; 5h - 80°C, 1h - 90°C; Ar; see Ref. [24.]

[#] Reaction conditions: 0.01g I/g-w; 0.09g monomer/g-w; 4h, 80°C; Ar; see Ref. [25.]

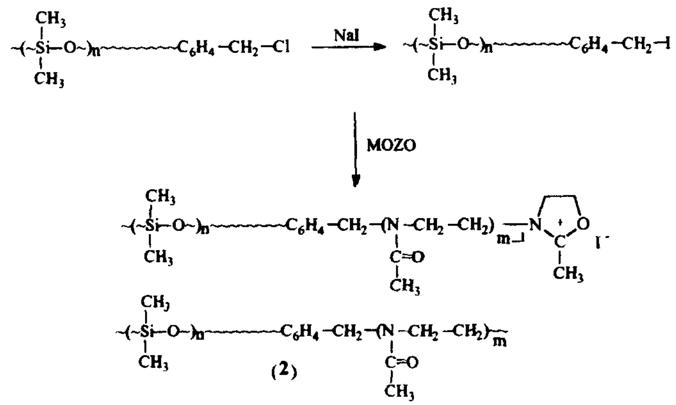
The polymerization of methacrylic acid in aqueous dilute solution initiated by PMOZO macroinitiators evidenced template features[26]. The peculiarities of the polymerization kinetics and the properties of the reaction products are strongly dependent on initiation procedure (photolysis or thermolysis), on the length of the PROZO sequence (the matrix), on monomer and overall concentrations.

Amphiphilic P(MOZO-vinyl) block copolymers were also found to act as efficient dispersants for ceramic materials such as silica (polymerization system: MMA/silica/PMOZO macroinitiator[25]). Composite materials with a homogeneous dispersion of the inorganic filler in the polymer matrix were thus obtained.

Cationic Polymerization of MOZO in the Presence of Chlorofunctional Polysiloxanes

The polymerization of 2-methyl-2-oxazoline initiated with chlorobenzyl groups end capped siloxane prepolymers (e PDMS-Cl) afforded the block copolymer (BSO) structure (**2**)[27] (Scheme 7) with excellent surfactant properties[28]. The use of polysiloxane with pendent functional benzyl chloride groups (c PDMS-Cl) gave graft copolymers (GSO) (Table IV).

A comparative study on the stabilization ability of the colloidal systems of the two types of copolymers evidenced that the emulsion polymerization kinetics is influenced by the non-ionic emulsifier nature (block or graft copolymer) and temperature, while particle diameter and polydispersity are dependent on copolymer structure, its composition and concentration. The block copolymers also proved surface modifier properties[29]. Their use in mixtures with commodity polymers (i.e. poly(butyl methacrylate)) gave flexible polymer films with improved UV stability, superficial hydrofobicity and adhesivity to polar supports, behaviour attributed to a peculiar morphology induced by the accumulation of the polysiloxane sequences at the polymer/air interface and of the PMOZO sequences at the polymer film/support interface.



SCHEME 7 Cationic polymerization of MOZO in the presence of PDMS-Cl.

TABLE IV Synthesis of poly(N-acetyliminoethylene)/polysiloxane block and graft copolymers[27]

Code	Copolymerization system*				Copolymer							
	Prepolymer†		MOZO	CHCl$_3$	N		PMOZO		DP PMOZO			Yield§
	type	(g)	(ml)	(ml)	(%)		(%)		theor.	calc††.		(%)
BSO$_1$	e PDMS-Cl	2.52	1.1	3.5	5.9		36.0		10	13.3		39
BSO$_3$	e PDMS-Cl	0.61	0.8	2.3	8.7		53.0		30	25.9		47
					A#	B#	A	B		A	B	
GSO$_1$	c PDMS-Cl	0.92	5.6	13.5	12.1	10.4	73.5	63.0	30	13.0	8.5	65
GSO$_2$	c PDMS-Cl	1.40	2.0	9.5	8.5	9.6	51.7	58.4	6	5.0	7.0	76

* Copolymerization conditions: 2h - 0°C, 46h - 54°C

† e PDMS-Cl: Mn = 3000, Mw/Mn = 1.35, Cl (%) = 1.79; c PDMS-Cl: Mn = 1120, Mw/Mn = 1.7, Cl (%) = 8.57

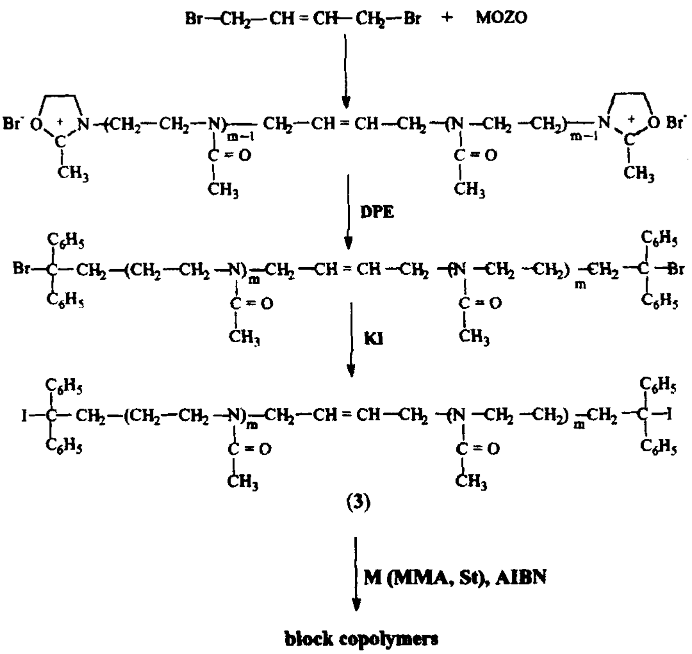
†† From N (%) and ^{1}H-NMR data

§ $(w_{PNAI} / w_{MOZO}) \times 100$

A - soluble fraction, B - insoluble fraction

Functional Polymers by Termination of Living PMOZO

Macromonomers and telechelics are important intermediates for the synthesis of functional polymers. End capping of living PROZO chains by appropriate nucleophiles is one of the most convenient and effective methods for their preparation[3-6,30]. The chain length can be in this case easily controlled by the polymerization feed $[M]_0/[I]_0$. By quenching the oxazolinium species with 1,1-diphenylethylene, telomers with the structure (3) were prepared. They can be used as macromolecular chain transfer agents in the radical polymerization of vinyl monomers to yield block copolymers (Scheme 8[31]).



SCHEME 8 Synthesis of MOZO telomers and poly(MOZO-vinyl) copolymers.

Macromonomers bearing styryl, (meth)acrylate, butadiene, acrylamide, vinylester or vinylbenzyl polymerizable groups were previously reported[3-6].

Most of them have been copolymerized with monomers with similar reactivity (styrene, meth(acrylate)s, vinyl acetate) giving rise to monodisperse small polymer particles[3-6,30] or to amphiphilic copolymers. Monodisperse, micronsized particles are used in a wide variety of domains ranging from coatings and adhesives to separation and calibration processes, biomedical, electronic and chemical industry. As an alternative to emulsion polymerization (successive seeded emulsion polymerization, soapless polymerization) the dispersion polymerization gained in interest in the last years. Recent papers report on the use of hydrophilic macromers as comonomers in such preparative processes[32,33]. Considering the possible and known uses of cinnamic acid and its derivatives in medical and cosmetics areas[34] we have synthesized PMOZO macromonomers with cinnamoyl end groups by end capping living PMOZO with cinnamic acid. The macromonomers (4) and (5) were used in dispersion polymerization.

C_6H_5-CH_2——PMOZO——OCO-CH=CH-C_6H_5 (4)
C_6H_5-CH=CH-COO——PMOZO-CH_2-CH=CH-CH_2-PMOZO——OCO-CH=CH-C_6H_5 (5)

As can be seen from Table V, the particle size and polydispersity are dependent on the applied polymerization technique and on macromer characteristics (PMOZO chain dimension, concentration). The photochemical polymerization seems to be a valuable synthetic alternative.

Other novel PMOZO materials were synthesized based on the same principle, using maleic acid as a nucleophilic quenching compound (Scheme 9). Depending on PMOZO chain functionality and on the molar ratio of maleic acid to oxazolinium species, two different macromers - (6) and (7) - or an unsaturated polyester (8) were obtained[31].

The development of the coupling reaction was followed by viscometric and conductometric techniques. Triethylamine and a copolymer based on poly(4-vinyl pyridine) were used as proton scavengers. The last one was proved to be more efficient and convenient. The products may be used in copolymerization

TABLE V Copolymerization of MOZO macromers with styrene[35]

Run	Macromer		Yield	Dispersion characteristics			
No.	Code*	%†	(%)	Dn (nm)	Dw (nm)	Dw/Dn	Stability††
1§	C_{30}	11	61	615	731	1.19	+
2§	C_{30}	3	68	951	1050	1.12	+
3§	C_{30}	2	57	710	2231	3.14	+
4§	C_{30}	0.7	38	-	-	-	-
5§	-	-	33	-	-	-	-
6#	C_{30}	2	51	952	1047	1.05	+

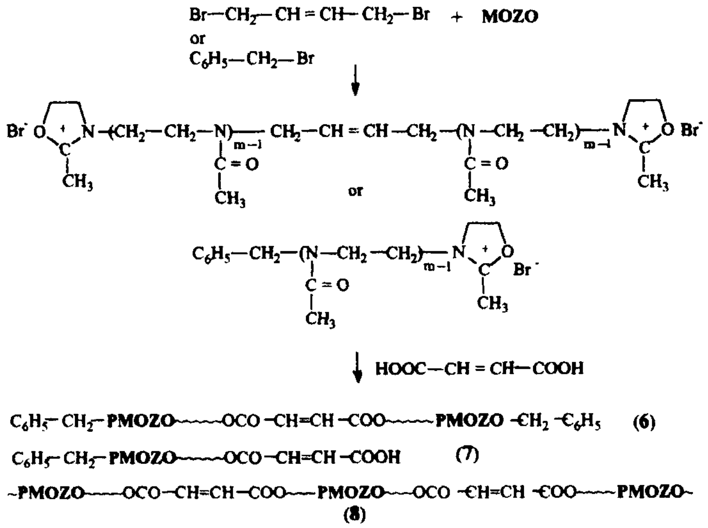
* C_{30} = macromer (4) with n = 30

† Weight % in macromer-styrene mixture

†† + stable, - unstable

§ Copolymerization conditions: 0.1g monomer/g solvent mixture; 3.10^{-2} g initiator/g solvent; solvent: 70/30 v/v ethanol/water; Ar; 6h, 70°C

\# Reaction conditions: 0.1g monomer/g solvent mixture; 3.10^{-2} g initiator/g solvent; solvent: 70/30 v/v ethanol/water; 6h irradiation with a high pressure mercury lamp of 500W situated at 16 cm from the quartz ampoule; Ar; 30°C



SCHEME 9 Synthesis of PMOZO containing main chain unsaturated units.

processes to obtain amphiphilic graft copolymers or polymeric networks. The carboxyl group of macromer (7) can be further transformed into new active functions or can serve for immobilization of enzymes[5].

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