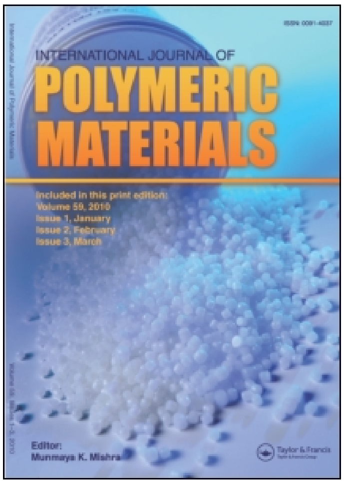

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Synthesis of Grafted Co-Polymers Based on N-Vinylcaprolactam and Low-Molecular Weight Siloxane Elastomers

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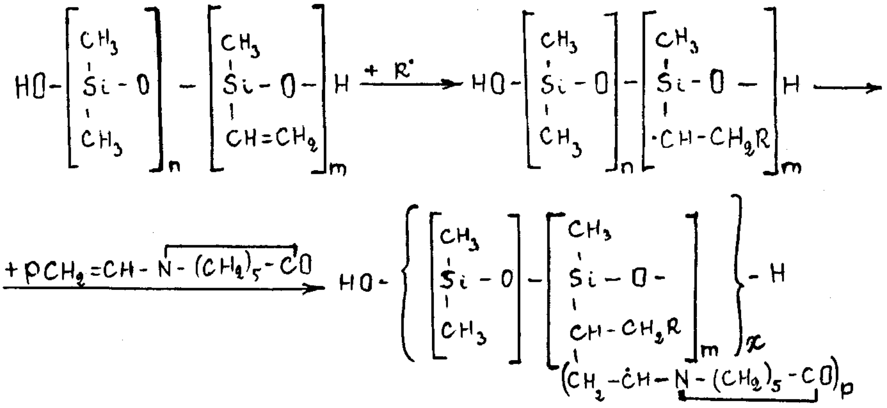
The grafting of N-vinylcaprolactam on vinyl groups containing low molecular weight siloxane elastomers is discussed. These hydrophylic graft copolymers are used in medicine.

KEY WORDS N-vinylcaprolactam, siloxane elastomers, graft co-polymerization medical applications.

So far, the siloxane elastomer-containing grafted co-polymers were well known,[1,2] but there is no information in the scientific literature about the grafting of N-vinylcaprolactam on vinyl groups containing low-molecular siloxane elastomers. Hydrophylic insoluble grafted co-polymers obtained in this are used as compositions for cold solidification used in medicine.[3] Grafting hydrogels on lisoxanes makes possible the mixing of different medicinal preparations with physiologically active materials.

The grafting of N-vinylcaprolactam and vinylethylether on vinyl containing low-molecular elastomers is carried out either in mass or in solvents, particularly in ethyl alcohol, as follows:

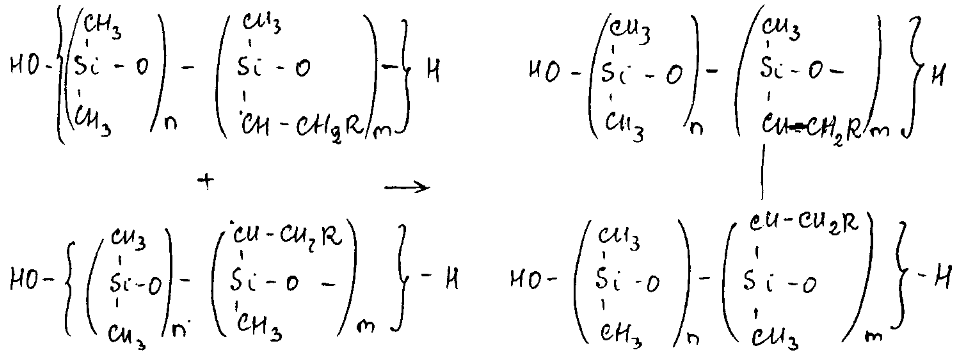


$$HO-\left[\begin{array}{c}CH_3\\ |\\ Si-O\\ |\\ CH_3\end{array}\right]_n-\left[\begin{array}{c}CH_3\\ |\\ Si-O-\\ |\\ CH=CH_2\end{array}\right]_m H \xrightarrow{+R^{\cdot}} HO-\left[\begin{array}{c}CH_3\\ |\\ Si-O\\ |\\ CH_3\end{array}\right]_n-\left[\begin{array}{c}CH_3\\ |\\ Si-O-\\ |\\ \cdot CH-CH_2R\end{array}\right]_m H \longrightarrow$$

$$\xrightarrow{+pCH_2=CH-\overline{N-(CH_2)_5-CO}} HO-\left\{\left[\begin{array}{c}CH_3\\ |\\ Si-O\\ |\\ CH_3\end{array}\right]_n-\left[\begin{array}{c}CH_3\\ |\\ Si-O-\\ |\\ CH-CH_2R\\ |\\ (CH_2-CH-\underline{N-(CH_2)_5-CO})_p\end{array}\right]_m\right\}_x-H$$

where R = $NC{-}C^{Me}_{Me}m$, m = 1,5; n = 98,5; p = 2,5,9,10,12; x = 2,3. Grafting is carried out during 4 hrs at 60–70°C temperature. Basic low-molecular siloxane elastomer contains 0,5–6,0% (mole) methylvinylsiloxane groups. The reaction is carried out in ethyl alcohol (20–30%) depending on the mass of reagents.

The created polymers are white viscous and amorphous masses with different viscosities, depending on the initial siloxane elastomers. If the reaction of grafting is carried out in mass, a space-structural gel-like material is obtained. Gel formation results from the sawing of chains of polyvinylcaprolactams. There is also a possibility that the reaction of structural polymers in the process of grafting of N-caprolactams on vinylcontaining siloxanes is caused by bridges of vinyl groups between siloxane chains.



In order to avoid gel formation, grafting of N-VCL* on V**-containing SE*** was conducted in an alcohol medium. When the reaction takes place in ethyl alcohol, the viscidly flowing polymers are easily obtained. Thus, grafting in an alcohol medium is a much faster process than grafting in mass. Systematic studies of the process of grafting have shown that the increase of the amount of grafting monomer produces a gel-like polymer and, in case of an increase in the amount of VS**** chains, the speed of grafting is increased and gel formation doesn't take place.

Among the tested three catalysts (H_20_2, Benz. peroxide, AIBN*****) in the 60–70°C interval, the most active centers were created with AIBN. Increased concentration of AIBN triples the grafting speed, but in an hour the differences among the curves becomes insignificant. The viscosity of grafted polymers was determined by the Gepler method. Usually, the viscosity of co-polymers created by grafting N-VCL on low-molecular vinylcontaining siloxanic elastomers is 7–10 times higher than the viscosity of basic elastomers when they contain 1,5% (mole) methylvinylsiloxane chains. If we increase to 60% the amount of N-VCL to be grafted, the viscosity of co-polymers will rise sharply and the grafted co-polymer will be obtained in a white powder state. The composition of homopolymer-polyvinylcaprolactams in grafted co-polymer was determined by the method of extraction.[3] Extraction was carried out by the vulcanizate of grafted co-polymers using the solvent dimethylformamid during 24 hrs. We used UV spectroscopy to determine N-VCL quantity.[4,5]

Investigations of the dependence of the grafting process on temperature have shown that heating a mixture of basic materials above 70°C, even using alcohol as a solvent, results in gel formation. However, at a temperature below 60°C the process is significantly slower. In the interval of 63 ÷ 67°C the grafting speed barely changes.

Irrespective of the amounts of N-VCL, all created co-polymers are vulcanazied at room temperature (cold solidification), as for ordinary liquid siloxane elastomers. Vulcanization proceeds by adding a mixture of TExSi****** and PbOct*******. If the amount of N-VCL is high (above 50%) in grafted co-polymer, then very viscous compounds are obtained. Mixed with catalysts, they are solidified immediately without time to take a desirable form, and they are not elastic.

Mechanical properties of grafted co-polymers' vulcanizers containing the different amounts of N-VCL are given in Table I.

The swelling experiment of the grafted co-polymers were carried out with many samples. Determination of swelling degree was followed until constant weight was reached. Investigation has shown the dependence of the swelling rate on the quantity of N-VCL in the grafted co-polymers. As expected, the swelling speed of vulcanizates is directly proportional to the amount of the grafted N-VCL. Vulcanizates containing more than 50% N-VCL during the swelling are disintegrated quickly because of the large amount of N-VCL. Physical and mechanical properties and swelling degree of the vulcanizates obtained on the basis of co-polymers are given in Table II.

After the first swelling of the samples, we cooled and dried them until they reached a constant weight and then put them back into the water to investigate their second swelling.

Thus, the physical and mechanical properties of vulcanizates of co-polymers

TABLE I

Physical-mechanical properties of grafted co-polymer vulcanizates containing N-VCL in different amounts grafted on low-molecular siloxane elastomers

Amount of the grafted N-VCL, %	Viscosity of the polymer, Pa-s	Physical-and-mechanical properties of the vulcanizates		
		Solidity limit at lengthening, p, kghr/cm2	Relative lengthening, %	Residual lengthening, l, %
5	1.60	0.05	55	0
15	2.95	1.30	120	0
20	3.66	2.00	150	0
25	4.54	2.70	150	0
30	7.26	2.90	130	0
40	9.80	1.20	85	0
50	38.66	2.5	50	0

TABLE II

Physical-mechanical properties and swelling degree of grafted co-polymer vulcanizates

				Physical-mechanical properties			
No polymer	Viscosity	Yield, %	Swelling capacity, %	Relative lengthening, %	Residual deformation, %	Tensile strength, %	Volatile products, %
Polymer No 1	71	85	25	200	5	8	7
Polymer No 2	84	83	24	250	5	12	6
Polymer No 3	93	87	27	260	5	15	5.5
Polymer No 4	105	89	30	300	5	18	5
Polymer No 5	154	86	31	310	5	22	5
Polymer No 6	214	90	35	335	5	49	5

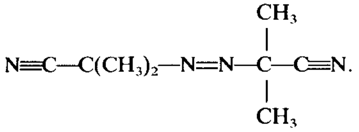
* N-vinylcaprolactam.

** vinyl.

*** siloxane elastomer.

**** vinyl siloxane.

*****



$N{\equiv}C{-}C(CH_3)_2{-}N{=}N{-}\overset{CH_3}{\underset{CH_3}{C}}{-}C{\equiv}N.$

****** Tetraethoxysilan.

******* Plumbum Octaet.

obtained by grafting of N-VCL on low-molecular vinylcontaining siloxane elastomers are equal or superior to the properties of other well-known similar compounds.

EXPERIMENTAL PART

Creation of the grafted co-polymer on the basis of N-VCL and vinyl-containing low-molecular siloxanic elastomers of different viscosities.

1. 7 g (70% of the whole mass) of low-molecular polysiloxane of the formulae: $HO\{[Si(Me)_2O]_n[SiMe(CH{-}CH_2)O]_m\}_xH$ ($\eta = 2.42$), 5 g (50%) of absolute ethyl alcohol and 0,03 g (0.3%) of AIBN were placed in a round-bottom flask with a mechanical mixer, reverse condenser, thermometer and a dropper funnel. The mixture was heated up to 60°C at constant mixing. At 65°C 3 g (30%) N-VCL was added in droplets from the funnel. The reaction mass was then heated for 4 hrs. The reaction began with the creation of white crystals and the increase in viscosity of the mixture was then observed. Samples were taken every 30 min to determine the viscosity. The mixture temperature was increased up to 70–80°C during 2 hrs in order to disintegrate the initiator (not taking part in the reaction). The residual alcohol and N-VCL were removed by distillation in vacuum. The residual mass was dissolved in $CHCl_3$ and was precipitated by means of absolute ether. 359,5 g of vulcanizate was separated. Its swelling capacity was studied for 1 month. Elemental analysis for the obtained co-polymer yielded (in %): C 36,85; H 7,92; Si 34,78; N 1,07. Calculated: C 37,07; H 8,25; Si 33,08; N 1,24. Swelling capacity: 30%. (Polymer No 1).

2. The reaction was carried out by the method described above. 7 g (η = 27) polysiloxane, 5 g (50%) absolute C_2H_5OH, 0.03 g (0,3%) AIBN and 3 g (30%) were mixed together. 151,62 g of white crystalline substance was separated for which the elemental analysis yielded: C 36,85; H 7,92; Si 34,78; N 1,07. Calculated: C 37,07; H 8,25; Si 33,08; N 1,24. Swelling capacity: 24% (Polymer No 2).

3. The reaction was carried out by the method described above. 7 g (70%) of polysiloxane (η = 30), 5 g (50%) of absolute C_2H_5OH, 0.03 g (0.3%) of AIBN and 3 g (30%) of N-VCL were mixed together.

135.7 g (87%) of white crystalline substance was obtained with $\eta = 93_{ps.min.}$ M 43363. Elemental analysis: Found: C 37.31%; H 7.87%; Si 31.94%; N 1.05%. Calculated: C 37.84%; H 8.27%; Si 32.29%; N 1.45%. Swelling capacity: 27%. (Polymer No 3).

4. The reaction was carried out by the method described above 7 g (70%) of polysiloxane (η = 55.3), 5 g (50%) of absolute C_2H_5OH, 0.03 g (0.3%) of AIBN and 3 g (30%) of N-VCL were mixed.

99.22 g (89%) of white crystalline substance was obtained with η = 105 M 46.000. Elemental analysis: Found: C 39,41%; H 7.94%; Si 29.82%; N 1.83%. Calculated: C 39,94%; H 8.34%; Si 30.11%; N 2.03%. Swelling capacity: 30%. (Polymer No 4).

5. The reaction was carried out by the method described above 7 g (70%) (η = 55.3) polysiloxane, 5 g (50%) of absolute C_2H_5OH, 0.03 g AIBN and 3 g (30%) of N-VCL were mixed.

99.22 g (89%) of white crystalline substance was obtained with $\eta = 105_{ps.min.}$. Elemental analysis: Found: C 39.41%; H 7.94%; Si 29.82%; N 1.83%. Calculated: C 39.84%; H 8.34%; Si 30.11%; N 2.03%. Swelling capacity: 31%. (Polymer No 5).

6. The reaction was carried out by the method described above. 7 g (70%) of polysiloxane (η = 60), 5 g (50%) of absolute C_2H_5OH, 0.03 g (0.3%) of AIBN and 3 g (30%) of N-VCL were mixed.

88.23 g (86%) of white crystalline substance was separated with $\eta = 154_{ps.min.}$ Elemental analysis: Found: C 40.07%; H 7.95%; Si 29.03%; N 1.93%. Calculated: C 40.58%; H 8.37%; Si 29.45%; N 2.21%. Swelling capacity: 35%. (Polymer No 6).

7. 2 g of grafted polymer, 6 drops of TExSi and 1 drop of PbOct were placed in a chemical glass and thoroughly mixed with a glass stick. The result was a solid mass, which was put in special rectangular glasses. In 20–24 hours a soft rubbery vulcanizate was obtained. The degree of swelling and physical and mechanical properties of the obtained vulcanizate were investigated (Table II).

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