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SYNTHESIS AND APPLICATIONS OF PHOTOCROSSLINKABLE POLYDIMETHYL SILOXANES—PART III. SYNTHESIS OF POLYSILOXANES WITH PERFLUORINATED AND ACRYLATED URETHANE LINKED PENDANT GROUPS

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Abstract—The synthesis of photocrosslinkable polysiloxanes containing perfluorinated pendant groups and that of acrylated groups linked by urethanes moieties was performed. The synthesis was carried out by copolycondensation of α,ω-dihydroxypolydimethylsiloxane and dichloro silanes bearing fluorinated and acetoxy groups. The acrylation was conducted by an ω-isocyanato-acrylate on the polysiloxane polyol prepared by acetolysis of the previous copolysiloxanes. The chain lengths are checked by addition of a monochlorosilane in order to obtain $\bar{M}_n$ values of about 10^4 mol/g. The influence of the fluorine content on the properties was investigated. Actually the critical superficial tension decreased from 25.5 to 21.0 and the T_g of the copolymer decreased to -120°C when a C_8F_{17} group was introduced. The use of these copolymers by u.v. curing was evaluated on sheets of aluminium, of PET and paper. The adhesion on these substrates are very good and release properties were studied, showing that incorporation of C_8F_{17} pendant group gave the best results.

INTRODUCTION

Since the seventies many works have been published on the synthesis of fluorinated polysiloxanes and the main ones have recently been summed up [1, 2]. The CF_3–$(CH_2)_2$ group is the most important pendant group used and a trifluoropropyl methyl polysiloxane is commercially available, mainly from Dow Corning Corp., but many researchers have introduced different fluorinated groups with longer fluorinated chains and also with other links between the siloxane chain and the fluorinated groups [1]. These polymers are crosslinkable by various ways, mainly thermically using SiH–Si vinyl system, but also via the hydrolysis of alkoxy groups $Si(OR)_x$. The former reaction is used for the synthesis of elastomers and Dow Corning [3, 4], Toray Silicone [5] and Shin Etsu [6] companies have investigated the synthesis of 'pumpable silicones'. The latter route is mainly used in coating (textile, leather, fibers . . .). The fluorinated group is obviously introduced to increase surface properties, solvent resistance, dielectric properties and chemical inertness. As for us, we previously synthesized the same kind of two components product (SiH–Si vinyl) [7, 8] by copolycondensation of α,ω-dihydroxydimethyl siloxane with dichlorosilanes bearing fluorinated groups $(CH_2)_3$–O–$(CH_2)_2$–C_nF_{2n+1} and SiH or Si vinyl groups. Other synthesis can be performed by anionic polymerization [9] mainly with low boiling point cyclosiloxanes $-(OSi(CH_3)(CH_2CH_2{-}CF_3))_x$ where $x = 3$ and 4. Another method of polymerization is the homopolymerization of an α,ω-dihydroxy fluorinated siloxane obtained by hydrolysis of the homologous dichlorosilane [10] as follows:

$$Cl_2Si(CH_3)(C_2H_4C_6F_{13}) \xrightarrow{NaOH} \alpha,\omega \text{ diol} \xrightarrow{Cat} \text{fluorinated siloxane.}$$

Various catalysts are used, e.g. stannous salts [11], alkaline metals [12] and complexes of tertiary amine with alcalino earthy salts [5].

The problem encountered for obtaining the materials is the curing, especially for the coatings which required time to provide hydrolysis silane. Thus, the introduction of lateral acrylic groups linked to the main chain by urethane groups was proposed [13] in order to obtain an u.v. or EB curing system. This work deals with the synthesis of photocrosslinkable polysiloxanes bearing fluorinated groups and acrylic groups, and the comparison of their properties with those of the corresponding nonfluorinated ones.

EXPERIMENTAL

The NMR spectra were recorded on a Bruker AC 250 apparatus using deutered chloroform as solvent.

The chemical shifts are given in ppm and the signals are noticed *s*, *d*, *t*, and *m*, respectively, for singlet, doublet, triplet and multiplet.

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IR spectra were taken with a spectrometer Perkin–Elmer 398, and the band positions are given in cm^{-1}, letters *w*, *m* and *st* standing, respectively, for weak, mean and strong intensities.

The fluorine content is determined by ionic chromatography on a Dionex series 2000 I apparatus.

The hydroxyl titration was made by a mixture of maleic anhydride–pyridine and the excess of anhydride and acid formed were titrated by sodium hydroxide.

The hydroxyl number is given by the following formula:

$$\%OH = \frac{(V_b - V_e)N_{NaOH} \cdot 17 \cdot 100}{1000 \cdot m_e}$$

with V_b, V_eNaOH volumes for the blank and the sample (ml).

N_{NaOH}: NaOH normality, m_e: weight of sample in g.

The isocyanate functions are titrated by dibutylamine in excess, and all excess is titrated by hydrochloric acid.

The NC=O content is given by the formula:

$$\%NC{=}O = \frac{(V_b - V_e)N_{HCl} \cdot 42 \cdot 100}{1000 \cdot m_e}$$

with the same meaning for the letters.

The contact angle between liquid and solid surface were measured by goniometer apparatus ERMA G-1 using the following process: a drop of liquid (water, CH_2I_2, glycerol or benzyl alcool) was deposited on the surface to study. The quantity of liquid was measured with a syringe monitored by amicrometric screw. We measured the angles starting from expanded figures.

The measurements were performed on cured products and the crosslinking was obtained under u.v. (80 W/cm^2 lamp).

Using Fowkes' law, the free superficial energy of solid and liquid can be separated into the dispersive component γ^d and the polar one γ^p. For the liquid $\lambda_L = \gamma_L^d + \gamma_L^p$ and for the solid $\gamma_S = \gamma_S^d + \gamma_S^p$. The basic Fowkes equation used is the Young–Dupre law $\gamma_S = \gamma_{SL} + \gamma_L \cos\theta$; where γ_S is the free superficial energy of the solid, γ_L is the free superficial energy of the liquid in equilibrium with its vapor and γ_{SL} is the free interfacial energy solid–liquid.

The T_G values are determined on 15 mg samples using a heating rate of 40°C/min on a Perkin–Elmer DSC apparatus.

Synthesis of III (8.9; 6)

In a two necked flask 50 g (0.073 mol) of I, 8.9 were introduced. We added, dropwise 12.69 g (0.0245 mol) of II, 6 and 9.22 g (0.0428 mol) of $AcO{-}(CH_2)_3{-}Si(CH_3)Cl_2$, 2.08 g (0.0122 mol) of $OSi(CH_3)_2Cl$ and 0.5 g of tetramethyl guanidinium salt.

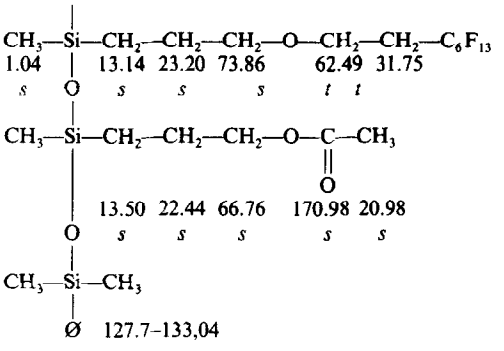
The mixture was magnetically stirred at 70°C for 18 hr, under a partial vacuum in order to eliminate the HCl formed during the reaction.

The mixture was diluted with ether, dried on Na_2SO_4, filtered and finally the solvent was evaporated under vacuum. The yield was almost quantitative.

^{1}H-NMR (described in the text).

IR (KBr). 2960 *st*; 2900 *st*; 2800 *w*; 1900 *w*; 1740 *st*; 1600 *w*; 1470 *w*; 1440 *w*; 1410 *m*; 1360 *m*; 1260 *st*; 1230 *st*; 1210 *m*; 1100 *m*; 1080–1000 (wide band) *m*; 970 *m*; 920 *w*; 900 *m*; 880 *m*; 860 *m*; 850 *m*; 800 *m*; 700 *w*.

^{13}C-NMR chemical shifts are attributed as follows:



Synthesis of compound IV (8.9; 6)

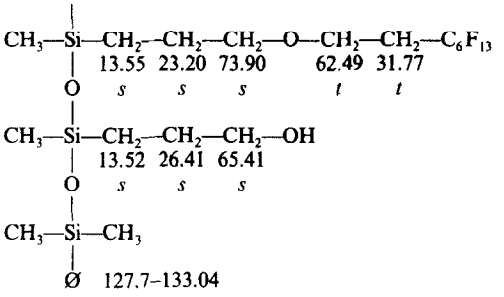
In a 250 ml flask 70 g of III (8.9; 6); 0.7 g (1%) of KCN and 60 ml of methanol were introduced.

The reaction was performed at room temperature under magnetic stirring for 24 hr. After washing (H_2O), drying and solvent evaporation, the product was characterized.

^{1}H-NMR (described in the text).

IR (KBr). 3350 (wide band) *w*; 2960 *st*; 2900 *m*; 2880 *m*; 1900 *w*; 1750 *w*; 1720 *w*; 1500 *w*; 1450 *w*; 1420 *w*; 1360 *st*; 1240 *m*; 1210 *m*; 1110–1010 *st*; 860 *m*; 800 *st*; 700 *m*.

^{13}C-NMR:



Synthesis of VI (4.49; 8)

In a two necked flask equipped with a condenser and N_2 inlet we introduce 12 g of IV (4.49; 8) (%OH exp. = 0.55%, %theor. = 0.71%), 1.22 g of V (NCO = 13.6%), 20 ml of toluene and 0.01 g of hydroquinone.

The mixture was heated at 50°C for 5 hr under mechanical stirring. After total disappearance of N=CO at 2280 cm^{-1} in IR, the $\emptyset CH_3$ was evaporated under vacuum and the compound VI was obtained in quantitative yield.

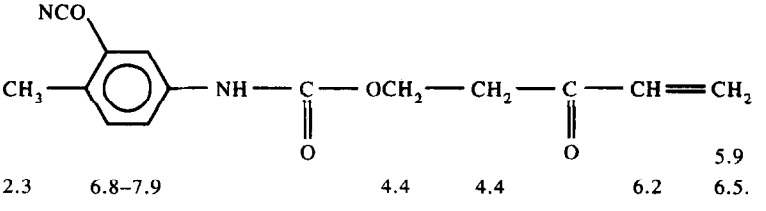
IR (KBr). 3340 *w*; 2990 *st*; 2950 *m*; 1740 *st*; 1620 *w*; 1540 *m*; 1450 *w*; 1410 *m*; 1370 *w*; 1260 *st*; 1270 *st*; 1150 *st*; 1110–1010 (wide band) *st*; 870 *m*; 800 *st*; 750 *w*; 710 *m*; 660 *w*.

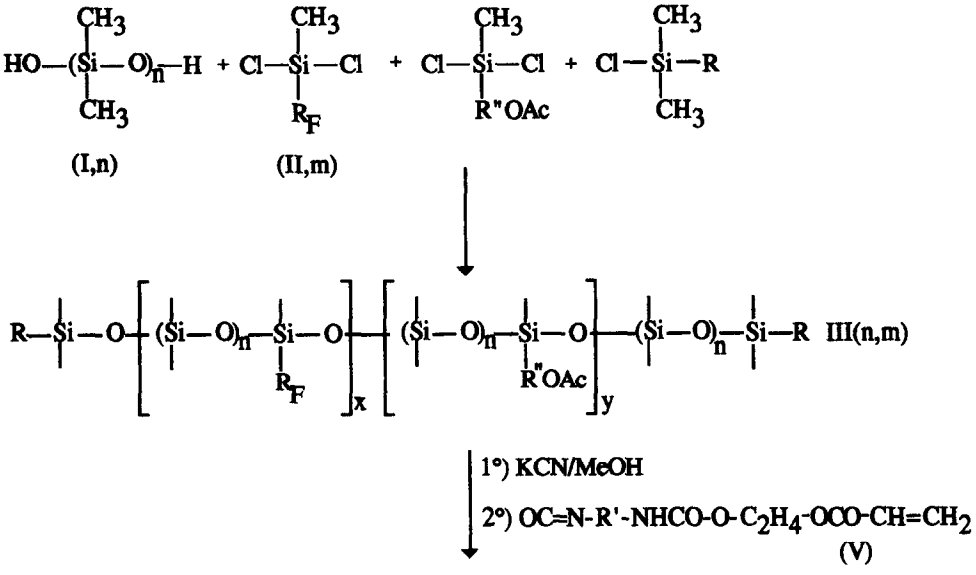
Synthesis of compound V

In a three necked flask, equipped with a condenser and N_2 inlet, we introduced 10 g of TDI, 0.1 g of DBDTL, 0.05 g of hydroquinone and 50 g of toluene, and through a dropping funnel, we added dropwise 6.6 g of hydroxy ethyl acrylate. The mixture was heated at 50°C for 5 hr.

The toluene was evaporated under vacuum, and the compound was obtained in quantitative yield.

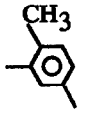
^{1}H NMR:

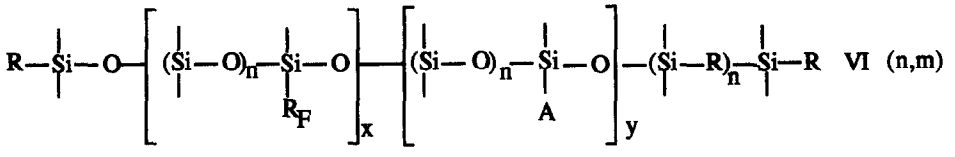




$R_F = (CH_2)_3—O—(CH_2)_2—C_mF_{2m+1}$ m = 6 and 8

R" = $(CH_2)_3$— ; R = Ø or $(CH_2)_3—OCOCH_3$

R' =  ; n = 4,49 and 8,9



A = $—(CH_2)_3—O—\overset{O}{\overset{\|}{C}}—NH—R'—NH—\overset{O}{\overset{\|}{C}}—O—C_2H_4—O—\overset{O}{\overset{\|}{C}}—CH=CH_2$

R" = Ø or A

Fig. 1. Reaction scheme of the synthesis of fluorinated photocrosslinkable polydimethyl siloxanes.

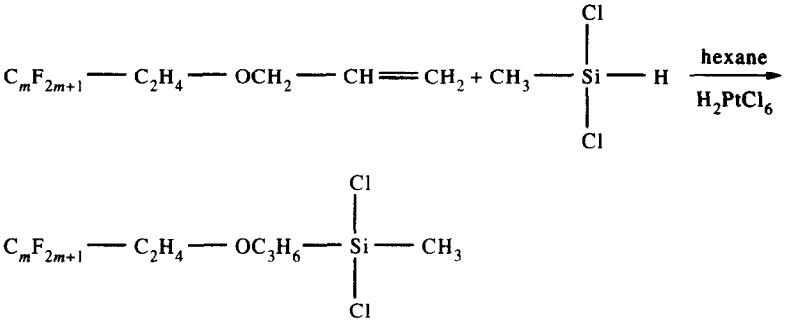
RESULTS AND DISCUSSION

The reaction scheme of the synthesis of fluorinated photocrosslinkable polydimethyl siloxanes is described in Fig. 1 and was performed in three steps. The first step is the copolycondensation, the second one concerns the hydrolysis of the acetal groups and the third one deals with the addition of ω-isocyanato acrylate. Before describing the synthesis of the copolymers, we describe the synthesis of their precursors. The dichlorosilane was prepared in two steps as follows:

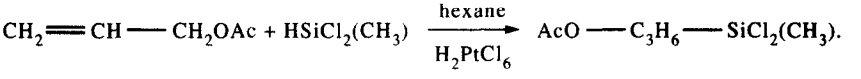
$$C_mF_{2m+1}—C_2H_4—OH + Cl—CH_2—CH=CH_2 \xrightarrow[NaOH\ (20\ N)]{TBAH} C_mF_{2m+1}C_2H_4OCH_2—CH=CH_2$$

m = 6 and 8.

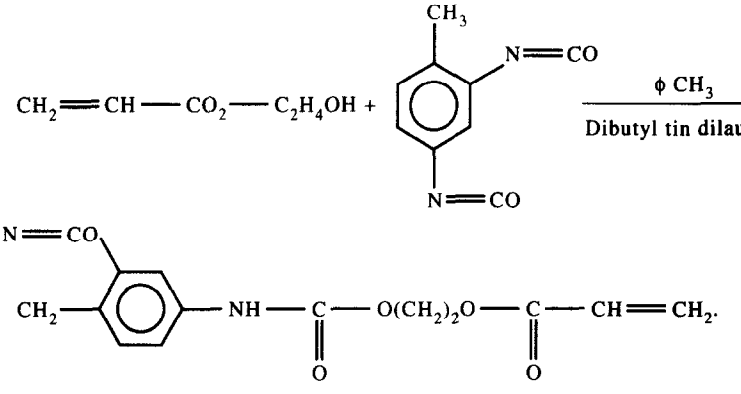
Experimental data have been previously patented [14] and published [15]:



The synthesis of these dichlorosilanes has already been described [16]. In the same way, the acetoxy propyl dichlorosilane was also prepared:



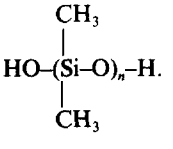
The ω-isocyanato acrylate has been prepared by Thomas *et al.* [17] as follows:



From these precursors, the synthesis of numerous polysiloxanes have been performed in various conditions.

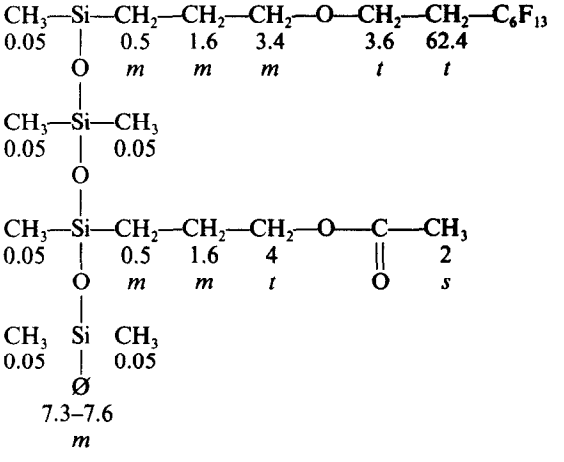
Actually, the fluorine content, the nature of chain ends, the number of curing groups and chain lengths are the parameters we have modified.

The characteristics of copolymerization are directed by the Flory's law, using an excess of chlorosilane over the α, ω-dihydroxysilane:



The chosen n values are 56, 8.9 and 4.49 in order to modify the $Si(CH_3)_2$–O content. The phenyl dimethyl monochlorosilane is used as limitating agent of molecular weight. The catalyst was salt of tetramethyl guanidine.

The content of each component after the reaction is determined by ^{1}H-NMR, considering the assignments of all the peaks as follows:



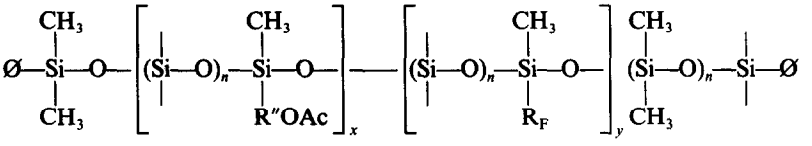
Actually, the ratio of acetate to fluorinated group is determined by the comparison of intensities of the methylene in γ position to the silicon atoms (at 3.4 and 4).

^{1}H-NMR allows us to check the molecular weight M_n using both phenyl groups by comparison to the total amount of $SiCH_3$.

Table 1. Main characteristics of urethane acrylate silicones (I–V)

Compounds	56/0/0/2.6 I	8.9/6/14.2/5 II	8.9/8/13.9/5 III	4.49/6/25/6 IV	4.49/8/30/6 V
$\bar{M}_n$(calculated)	9540	13650	14350	9840	10740
Number of unsaturations	3	6	6	4	4
Number of (Si–O) groups	115	120	120	67	67
Curing site (%)	2.6	5	5	6	6
Fluorine content (%)	0	14.2	13.9	25.0	30.0

So, the expected structure of such a product can be proposed according to the following formula:



with $R'' = (CH_2)_3$– and $R_F = (CH_2)_3—O—(CH_2)_2—C_mF_{2m+1}$.

For each prepared and characterized product a nomenclature of the products was chosen as follows:

$$n/\text{number } m/\%F/\% \text{ curing site}$$

with, when R = A

$$\% \text{ curing site} = \frac{x+2}{(n+1)x+(n+1)y+n+2}\,\%$$

and when $R = \text{Ø}$

$$\% \text{ curing site} = \frac{x}{(n+1)x+(n+1)y+n+2}\,\%.$$

The results obtained for four fluorinated products with various fluorine contents (from 5 to 30%) and one nonfluorinated silicone are gathered in Table 1 in order to compare the properties.

The second step of the synthesis was the hydrolysis of the acetyl group performed in the presence of methanolic KCN at room temperature for 24 hr.

The ^{1}H-NMR permits the control of the decrease of the CH_3 in the acetyl group at 2 ppm and the increase of the methylene group adjacent to the hydroxy group at 3.7 ppm which replaces the previous methylene at 4 ppm. It was observed that the hydrolysis was never complete (70% maximum). Besides, the hydroxyl index obtained was 0.72% whereas the expected theoretical value is 1.07%.

The last step is the acrylation, with isocyanato (V) previously described, in toluene at 50°C for 5 hr in the presence of hydroquinone in order to avoid polymerization of the obtained polyacrylate.

In the ^{1}H-NMR spectrum of these compounds (Fig. 2), the hydrogen of CH_3–Ø shifted to 2.2–2.4 ppm, –COO–CH_2 to 4.4 ppm and CH_2=CH– both to 5.8 and 6.6 ppm. The aromatic protons within TDI systems possessed the chemical shift at 7.0–7.3 ppm.

In the same way, IR spectra show disappearance of N=CO groups at 2280 cm^{-1} since we had a stoichiometric amount of isocyanato acrylate (V) towards hydroxyl group of product IV (n, m).

In a second time, we have studied and compared the properties of the obtained multiacrylate on various formulations of cured products using the following process: 60% of multiacrylate, 40% of $CHCl_3$ were mixed and we added 4% of Darocur 1173, 2% of isopropyl thioxanthane (ITX) and 2% of ethyl-4-dimethyl amino-benzoate EDB (relative to the first mixture).

After stirring, the mixture is poured in an aluminum cupel and iradiated (after removing $CHCl_3$) under u.v. with a 80 W/cm^2 lamp. First, we have studied the surface properties of three compounds. We have noted the influence of the fluorinated groups incorporation on the properties where the critical superficial tension decreased from 25.5 to 21 dyn/cm (Table 2).

Table 2. Influence of fluorinated groups on surface properties of urethane acrylate silicones

	Water/diiodomethane		
	γ_s^d(dyn/cm)	γ_s^p(dyn/cm)	γ_s(dyn/cm)
56/0/0/2.6	23.2	2	25.5
8.9/6/14.2/5	22.9	2.2	25.1
8.9/8/13.9/5	20.4	0.7	21.1

Table 3. Glass transition temperatures of prepolymers and synthesis polymers

Compounds	T_g(°C)
*Trifluoropropyl methyl polysiloxane	−63
*HO–$(Si(CH_3)_2O)_n$–H; $n = 4.49$ 4.49/0/0/0	−99
*HO–$(Si(CH_3)_2O)_n$–H; $n = 8.9$ 8.9/0/0/0	−115
4.49/6/25/6	−101
4.49/8/30/6	−116
8.9/8/14/5	−120

Table 4. Test results on various urethane acrylate silicones after u.v. irradiation

Compounds	Square pattern	Scotch test	Solvent test	Impact resistance 400 g	Impact resistance 1000 g
56/0/0/2.6	5	5	90	50 cm	
8.9/6/14.2/5	5	5	120		> 50 cm
8.9/8/13.9/5	5	5	80		> 50 cm
4.49/6/25/6	5	5	70		> 50 cm
4.49/8/30/6	5	5	70		50 cm

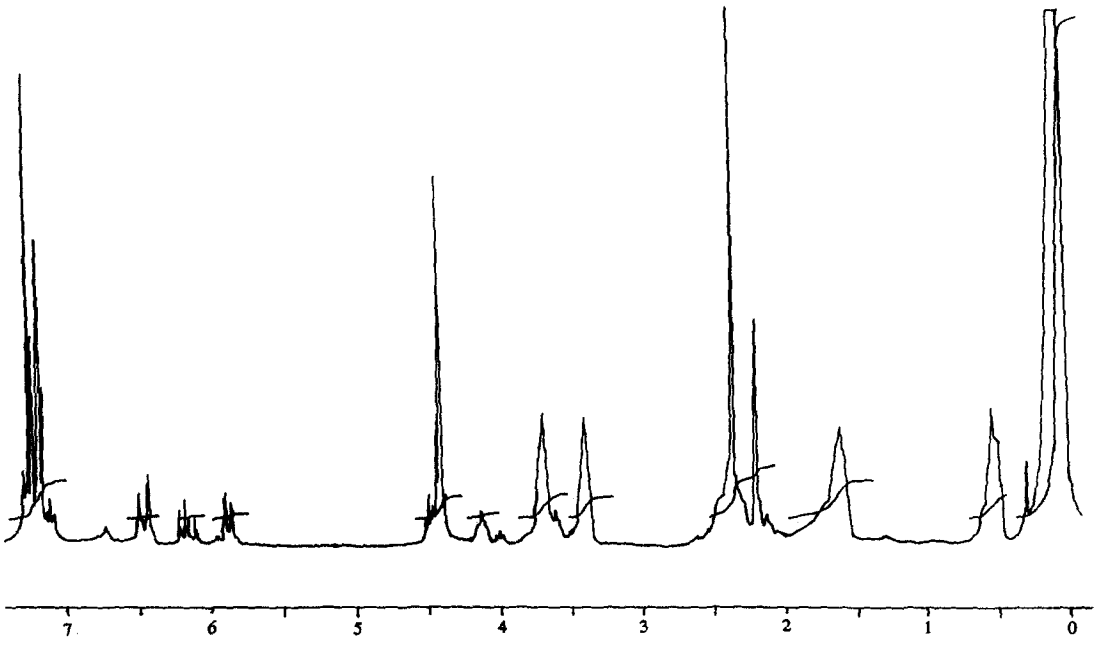


Fig. 2. ^{1}H-NMR of compound VI (4.49; 8).

Then, we studied the values to T_G depending on the compositions of formulations made with the same procedure as above. The results are gathered in Table 3. This table shows that the length of the silane diol is a very important parameter, the longer the silane, the lower the T_G.

It is also important to notice that when we increase the length of the fluorinated chain, the T_G value decreases.

So, it is possible to obtain a highly fluorinated silicone (30%) with a very low T_G (−120°C).

In the last part of this work we have studied three applications of these compounds: coatings on aluminium, on paper and on polyethylene terephtalate (PET).

Coating on aluminum

The formulations containing the previous products are spread with a Hand Coater on aluminum sheets with 12 μm of thickness. The films are evaporated and cured by u.v. lamp until they are dry to touch.

The different tests performed on these films are the following.

Adhesion. First, a square pattern (the square area is 1 mm^2) is made with a cutter on the coating. Then, we note whether the film is flaked off. The mark is 0 if all the squares have been flaked off, and 5 if no squares have been taken off.

Second, we performed a scotch test: scotch tape is stuck on the former square pattern, and it is pulled up. If the film sticks on aluminum, the mark is 5/5, whereas for a taken-off film, the mark is 0.

Solvent resistance. We used methyl ethyl ketone (MEK) for this test. Several round trips of cotton saturated with this solvent are executed. We count the number of runs until the aluminum sheet appears. Up to 100 runs, the coating resists the solvent.

Impact resistance. A weight falls down from different heights onto a template (coating + aluminum sheet), and we measure the level at which the film begins to take off. The maximum height usable with our apparatus is 50 cm.

The results of these tests are gathered in Table 4. It can be observed that the spreading and the brightness are excellent. The very good strength to the scotch test after squaring is shown by the absence of scales during tear stress. It can be noticed that all our films present a very good impact resistance. Finally these films present good adhesion on aluminum. On the contrary our coatings have poor strength to MEK except the compound (8.9/6/14.2/5). The samples are also subjected to a postcoating and the results of the tests are the same as previously. The only solution to improve the solvent resistance consists of increasing the thickness of the film to 24 μm.

However, the bests results are obtained with the products (8.9/6/14.2/5) and (8.9/8/13.9/5) which contain a mean content of fluorinated group and the disilanol with 8.9 units of $-Si(CH_3)_2O-$.

Coating on paper

The purpose of this application is the release paper. In this case it is necessary to decrease the strength to separate a piece of scotch from the covered paper, and on the other hand these properties should remain after aging. We used the same formulations as for aluminum and they were spread with a hand coater in order to obtain a layer 4 μm thick.

The curing was performed by an u.v. lamp of 80 W/cm^2.

The tests of adhesion were made as usually and we obtained a very good release paper which can be classified in increasing order as follows:

$$I < II \quad III < IV < V.$$

Coating on polyethylene terephtalate (PET)

In the same manner, the coating mixtures were applied on PET and exposed to a u.v. lamp (80 W/cm^2). The release properties are better than those obtained on paper.

CONCLUSION

The introduction of perfluorinated groups in photocrosslinkable silicone chains was performed by copolycondensation between an α,ω-dihydroxy polydimethylsiloxane, 3-acetoxy propyl methyl dichlorosilane and perfluorinated silanes. After hydrolysis of the obtained product, the grafting of an acrylic monomer that contains an isocyanate end group onto primary hydroxy functions was performed. The physicochemical properties of u.v crosslinked products were studied. T_gs are similar to those of PDMS (-120 and -100°C) whereas basic $-[Si(CH_3)(C_2H_4CF_3)O]-$ fluorinated silicones have a T_g of about -63°C. Surface properties were improved for greater fluorinated chains, for which superficial tensions were decreasing from 25 to 21 dyn/cm.

Several applications were investigated, especially for release properties. Actually, they are much better when the siloxane chain lengths are higher. However, the fluorinated groups do not bring oustanding improvement for that application.

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