Chemistry

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Abstract

Full Text

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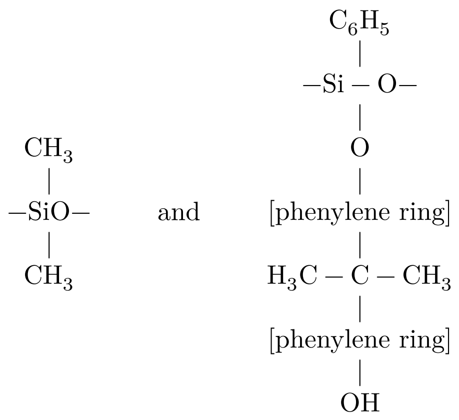
On the Directed Modification of the Properties of High-Molecular Compounds

The problem of the purity of monomers and the associated quality of polymers is a very urgent one. Impurities that interfere with directed reactions for the formation of large molecules of the desired structure exert a negative influence on the properties of polymers, commensurate with their quantity. The necessity of using pure monomers in order to obtain polymers with high technical properties is quite obvious. If disruption of the size and structure of large molecules by insignificant amounts of impurities leads to a sharp deterioration in the properties of a polymer, then it should be expected that the introduction into molecules, in microdoses, of elements or groups differing in composition should exert a positive influence on the properties of polymers. Directed modification of the properties of polymers requires establishing the relationship between the polymer and the elements or groups introduced into its composition and the properties of the new polymer obtained. The problem of directed modification of the properties of polymers by introducing, into the chain in microdoses, elements or groups of composition different from that of the main molecular chain is not being studied.

In the present work, the influence was studied of various elements and groups introduced in microdoses into the main chains of polymer molecules on mechanical and elastic properties, thermo-oxidative stability, and adhesive properties. As the basic polymers, polymers with inorganic main molecular chains were taken: 1) with linear molecular chains of the composition:

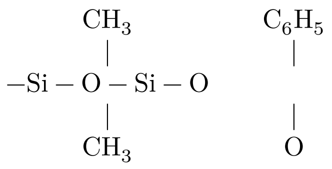


$$\begin{array}{c}CH_3\\|\\-SiO-\\|\\CH_3\end{array}\quad\text{and}\quad\begin{array}{c}C_6H_5\\|\\-Si-O-\\|\\O\\|\\\text{[phenylene ring]}\\|\\H_3C-C-CH_3\\|\\\text{[phenylene ring]}\\|\\OH\end{array}$$

Polydimethylsiloxane

Polyphenyl-(oxyphenylpropylidenephenoxy)-siloxane

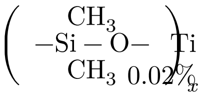
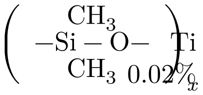
2) polymers with branched molecular chains of the following composition:



$$\begin{array}{ccc}&CH_3&&C_6H_5\\&|&&|\\-Si-O-&Si&-O&\\&|&&|\\&CH_3&&O\end{array}$$

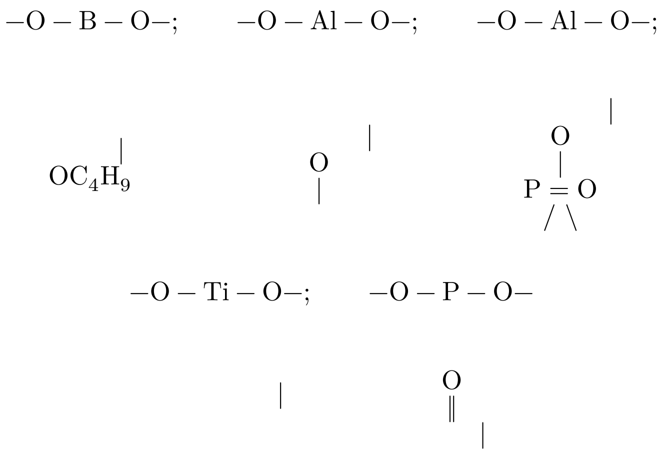
Table 1

Polymer chain unit	Introduced element, %	Indices	0	2	3	4	5
$\left(\begin{array}{c}CH_3\\-Si-O-\\CH_3\end{array}\right)_x$	0	a	45.6	40.3	36.9	32.5	Specimen brittle
$\left(\begin{array}{c}CH_3\\-Si-O-\\CH_3\end{array}\right)_x$	0	b	325	108	150	33	Specimen brittle
$\left(\begin{array}{c}CH_3\\-Si-O-\\CH_3\end{array}\right)_x$	0	c	4	0	0	0	Specimen brittle
$\left(\begin{array}{c}CH_3\\-Si-O-\\CH_3\end{array}\right)_x$	Ti 0.02%	a	57.0	46.9	44.4	46.0	46.1

Polymer chain unit	Introduced element, %	Indices	0	2	3	4	5
 $\left(-\overset{CH_3}{\underset{CH_3}{Si}}-O-\right)_x$	Ti 0.02%	b	637	150	100	75	53.0
 $\left(-\overset{CH_3}{\underset{CH_3}{Si}}-O-\right)_x$	Ti 0.02%	c	15	3	0	0	0

Note. a $-P$ in kg/cm^2; b $-L$ in %; c $-l$ in %.

Polydimethylpolyphenylsiloxane. In the work, the following elements introduced in "microdoses"were studied: boron, aluminum, titanium, and phosphorus, which were introduced into the chain —Si—O—Si—in the form of the following groups:



$$-O-\underset{OC_4H_9}{\underset{|}{B}}-O-;\qquad -O-\underset{\underset{|}{O}}{\underset{|}{Al}}-O-;\qquad -O-\underset{\underset{/\ \backslash}{\underset{P=O}{\underset{|}{O}}}}{\underset{|}{Al}}-O-;$$

$$-O-\underset{|}{Ti}-O-;\qquad -O-\underset{|}{\overset{\overset{O}{\|}}{P}}-O-$$

Titanium was added to polydimethylsiloxane in an amount of 0.02% in the form of the group

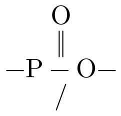
$$-O-Ti-O-Si-$$

with the aim of increasing the thermooxidative stability of the polymer.

Fig. 1. Aging of rubbers at 300° as a function of various additives.

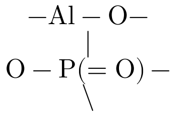
Experiments showed that the properties of the polymer changed sharply when rubber specimens were tested (Table 1). The thermooxidative stability increased considerably, and the mechanical and elastic properties of the polymer increased.

A change in the properties of the polydimethylsiloxane elastomer is also observed upon introduction of 0.02% phosphorus in the form of the group



$$-\underset{/}{\overset{\overset{\displaystyle O}{\|}}{P}}-O-$$

As is seen from Fig. 1, the thermooxidative stability of rubbers containing phosphorus (curve 1) is considerably higher than that of rubbers made from pure polydimethylsiloxane elastomer (curve 2). Phosphorus has the same effect on elongation (curves 3, 4). The introduction into the polydimethylsiloxane elastomer of aluminum in an amount of 0.01% and phosphorus in an amount of 0.015% in the form of the group

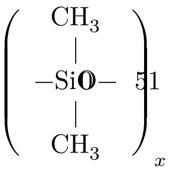


$$\begin{array}{c} -Al-O- \\ | \\ O-P(=O)- \\ \backslash \end{array}$$

led to a significant improvement of the ela-

···mechanical properties and their preservation at a higher level than in the control specimens during prolonged heating in air (Table 2).

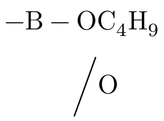
Table 2

Polymer chain unit	Introduced element, %	Normal conditions: a	Normal conditions: b	Normal conditions: c	After aging in air (in days) at 250°: 3: a	3: b	3: c	8: a	8: b	8: c	20: a	20: b	20: c
 $\left(-\underset{CH_3}{\overset{CH_3}{\overset{\vert}{\underset{\vert}{Si}}}}O-\right)_x$	0	51	100	0	36	80	5	40	50	5	30	50	0

Polymer chain unit	Introduced element, %	Normal conditions: a	Normal conditions: b	Normal conditions: c	After aging in air (in days) at 250°: 3: a	3: b	3: c	8: a	8: b	8: c	20: a	20: b	20: c
$\left(-\underset{CH_3}{\overset{CH_3}{\overset{\vert}{\underset{\vert}{Si}}}}-O-\right)_x$	Al 0.01%; P 0.015%	49	252	5	60	375	5	54	307	5	48	170	5
$\left(-\underset{CH_3}{\overset{CH_3}{\overset{\vert}{\underset{\vert}{Si}}}}-O-\right)_x$	Al 0.02%; P 0.03%	51	600	10	53	350	6	52	250	5	44	200	5

Note. a $-P$ in kg/cm^2; b $-L$ in %; c $-l$ in %.

Into polyphenyl-(oxyphenylpropylidenephenoxy)-siloxane, in order to change the adhesive properties and increase thermal stability, boron was introduced in the amount of 0.05% in the form of the group

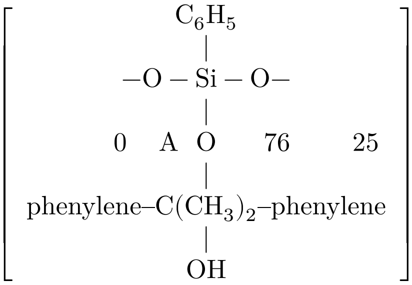


$$-\underset{\diagup O}{B}-OC_4H_9$$

in a polydimethylborsiloxane elastomer (specimen V) and 0.3% in a polyphenylmethylborsiloxane elastomer (specimen G).

Table 3

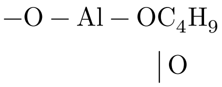
Adhesive properties of polymers

Polymer chain unit	Introduced element, %	Specimen	Shear strength, kg/cm²: at 25°	Shear strength, kg/cm²: at 425°	Shear strength after thermal aging: 4 hours at 425°; tests at 20°	Shear strength after thermal aging: 4 hours at 425°; tests at 425°	Shear strength after thermal aging: 24 hours at 300°; tests at 20°	Shear strength after thermal aging: 24 hours at 300°; tests at 425°	Shear strength after 10 days of water exposure at 20°: tests at 20°	Shear strength after 10 days of water exposure at 20°: tests at 425°
 $\left[-O-\overset{C_6H_5}{\underset{O-\text{phenylene}-C(CH_3)_2-\text{phenylene}-OH}{Si}}-O-\right]$	0	A	76	25	32	19	22	17	61	19.5
Same	0	B	63	27	10	15	8	13	45	24
Same	B 0.05%	V	93	36	71	43	68	40	81	38
Same	B 0.3%	G	151	38	101	42	80	42	not determined	not determined
Same	Ti 0.16%	E	110	51	30	32	67	41	106	52
Same	Al 0.12%	I	56	24	36	42	47	34	49	40

Along with this, into polyphenol-(oxyphenylpropylidenephenoxy)-siloxane there were introduced: 0.16% titanium in the form of the group

$$-O-Ti-O-Si-$$

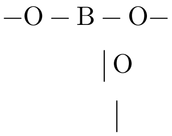
in polydimethylsiloxane (sample E), and 0.12% aluminum in the form of the group



$$\begin{array}{l} -O-Al-OC_4H_9 \\ \qquad\quad |\,O \end{array}$$

in polydimethylsiloxane (sample I). As can be seen from Table 3, samples V, G, and E, in comparison with controls A and B, have higher adhesive properties and thermal stability.

The adhesive properties were sharply increased by introducing 0.03% boron in the form of the group

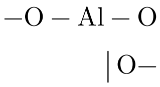


$$\begin{array}{l} -O-B-O- \\ \qquad |\,O \\ \qquad\ | \end{array}$$

into a polydimethylsiloxane elastomer.

The resulting polybordimethylsiloxane formed self-adhesive rubber specimens, in contrast to polydimethylsiloxane elastomers, which, as is known, do not possess self-adhesive properties.

Experiments with polymers having branched molecular chains also showed that the introduction of small amounts of aluminum in the form of the



$$\begin{array}{l} -O-Al-O \\ \qquad\ |\,O- \end{array}$$

group leads to a considerable increase in the thermal stability of the polymer.

Films of polydimethylpolyphenylsiloxane containing 0.05% aluminum, as can be seen from Table 4, had higher thermo-oxidative stability in comparison with the pure polymer.

Table 4

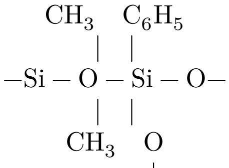
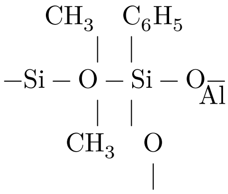
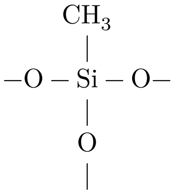
Polymer chain unit	Introduced element, %	Weight loss of polymer films after heating, 24 h	Weight loss of polymer films after heating, 72 h	Weight loss of polymer films after heating, 360 h
 $-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{O}{\overset{C_6H_5}{Si}}-O-$	0	12.0	17.2	22.0
 $-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{O}{\overset{C_6H_5}{Si}}-O-$	Al, 0.05%	5.0	8.4	10.0

Table 5

Polymer chain unit	Introduced element, %	Weight loss after heating polymer at 400°, 1 h	Weight loss after heating polymer at 400°, 5 h	Weight loss after heating polymer at 400°, 15 h
 $-O-\underset{O}{\overset{CH_3}{Si}}-O-$	0	10.0	11.5	–
Same	Al 0.05%	3.2	6.0	6.5

A similar result was obtained when 0.05% aluminum was introduced into polymethylsiloxane (Table 5).

Consideration of the experimental data obtained confirms the possibility, by introducing insignificant amounts of substances differing in chemical composition from the principal polymer, of directionally changing the properties of polymers. In this unexplored field, significant theoretical and practical results should be expected in the coming years.

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