Graft Polymerization of Octafluoropentyl Acrylate on Polycaproamide Thread

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ABSTRACT: Octafluoropentyl acrylate [H(CF$_2$CF$_2$)$_2$CH$_2$-C(O)CH=CH$_2$] and polycaproamide (PA-6) thread were copolymerized with a *tert*-butyl hydroperoxide initiator. The fluorine content of the thread was 0.87–1.33% after copolymerization. The creation of ester polyfluorinated alkyl groups on the end of the polyamide macromolecules by the homolytical substitution of hydrogen atoms in the α-CH$_2$— group of the —HN—CH$_2$—(CH$_2$)$_4$—C(O)— chain led to an increase in the tensile strength of the PA-6 thread. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4028–4029, 2006

INTRODUCTION

Fluoroacrylate was previously graft polymerized on the surface of polycaproamide (PA-6) by a plasma method.[1] This led to an increase in the flame resistance of PA-6. Material modified by polyfluorinated compounds has waterproof and dustproof properties.[2] A lack of graft polymerization of monomers to PA-6 usually leads to a decrease in its tensile strength.[3,4] Octafluoropentyl acrylate [H(CF$_2$CF$_2$)$_2$CH$_2$OC(O)CH=CH$_2$ (**I**)] was obtained from octafluoropentyl alcohol[5] to produce 1.1.3-trihydroperfluoropropanol for the production of laser disks.[5] Therefore, the use of octafluoropentyl alcohol is important. Peroxide and laser methods[1] for the initiation of graft polymerization differentiate selective polymerization because there is usually mild copolymerization with the *tert*-butyl hydroperoxide (**II**) initiator.

The object of this investigation was the graft polymerization of **I** on the surface of PA-6 under conditions of the minimum homopolymerization of monomer and the production of a fluorinated thread with a high tensile strength.

EXPERIMENTAL

I was obtained by the method in ref. 5. The boiling point was 85°C (pressure vacuum = 40 mmHg; n_d^{20} = 1.3462; d_4^{20} = 1.4460). The PA-6 thread (14.54 tex) samples were 1.2–1.5 m long. They were plunged into a 1% solution of **II** in **I** and were thermostated at 80°C for 1–4 h (surplus of monomer = 1 : 75), with the fluorine content in the PA-6 thread and the physicomechanical properties analyzed every hour.

RESULTS AND DISCUSSION

The reaction of **I** and PA-6 was initiated by **II**. The destruction[6] of **II** gave (CH$_3$)$_3$CO · and HO · radicals, which tore away α-hydrogen atoms from —NH—CH$_2$(CH$_2$)$_4$C(O)— groups of the macromolecule PA-6 to form macroradical **III** (Scheme 1).[7–9]

III has nucleophilic properties. Therefore, it added electrophilic CH$_2$=CH— groups of **I** across the cyclic structure **IV,** which permitted associative interactions between H$_2$N end groups in **III** and associated O=C— groups of **I.** The electronic density was delocalized in **IV** by double bonds, associated O=C— groups, and fluorine atoms of the perfluorinated groups (Scheme 2).

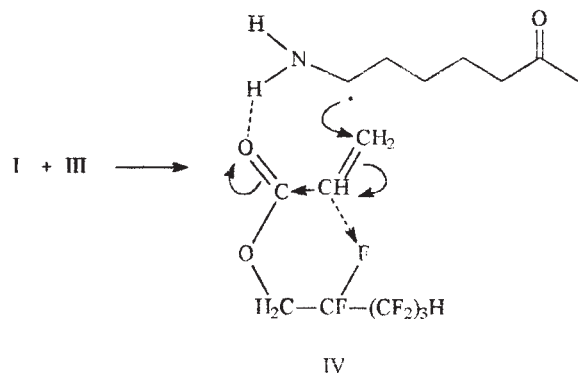**IV** was reorganized by macroradical **V** (Scheme 3).

The stability of **V** was possible because the electronic density was delocalized on associated O=C— groups and perfluorinated groups in the bicyclic sys-
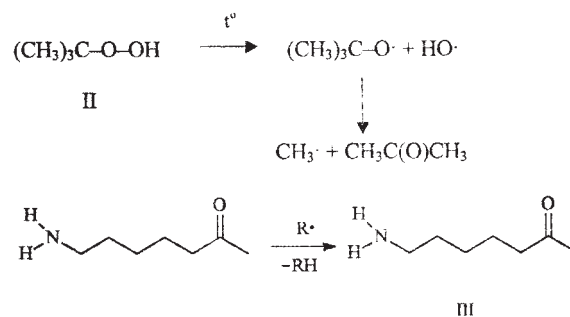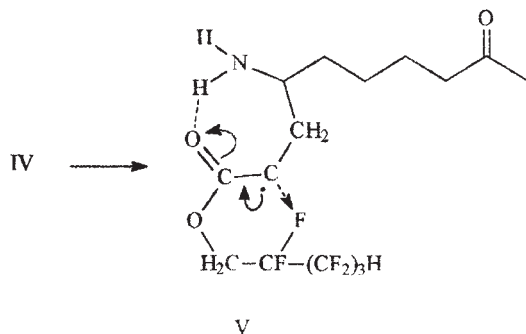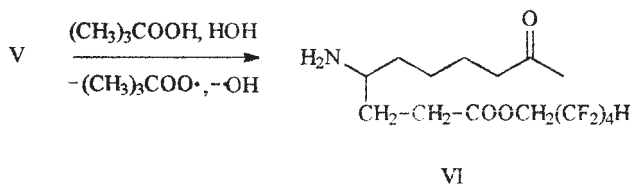
Scheme 1

Scheme 2

tem. The interaction of **V** with new molecules of the polyfluorinated monomer may have been difficult. However, **II** and water molecules reacted with **V** to give α-polyfluorinated PA-6 (Scheme 4).

Graft polymerization was proven by the increasing tensile energy of the PA thread (Table I).

The graft polymerization of acrylates to PA-6 usually leads to a decrease in the tensile strength of the PA-6 thread. The increase in the tensile strength for **I** may be explained when one considers the mechanism of the graft polymerization of **I**. The mechanism includes the participation of end-group macromolecules of PA-6. As far as it may be seen from the cyclic structure (because of the associative interactions), the end groups increase the degree of molecular orientation in the amorphous phase of the polymer, which usually leads to an increase in the tensile strength. The proof of participation of the end groups was the fluorine content in the modified PA-6 thread (Table II).

Scheme 3

Scheme 4

TABLE I
Changes in the Physicomechanical Properties[a] of the Initial PA-6 Thread and Treated Polyfluorinated Acrylate, IPA-6 Thread

Time of graft polymerization (h)	Tensile strength (N)	Tensile elongation (%)	Retained tensile elongation (%)
0	9.1	14.4	4.6
1	9.4	16.5	6.6
2	9.3	15.6	6.2
3	9.3	14.0	5.5
4	9.7	21.8	8.7

[a] The average was obtained from five experiments.

TABLE II
Fluorine Content in the Modified PA-6 Thread

Time of modification (h)	Fluorine content (%)
2	0.87
3	1.19
4	1.33

The fluorine content in the PA-6 thread did not change much in the time of modification. One peculiarity of the graft polymerization by **II** of the initiator was the absence of a considerable quantity of homopolymer. This was due to the active interaction of macroradicals (**III**) and radicals from the polyfluorinated monomer, which led to the precipice of chains. The kinetics of polymerization of methyl methacrylate in the presence of modeled compounds with —NH—$(CH_2)_5$—C(O)— groups is related to the chain-propagation reaction constant to the chain interruption constant less in two times.[8]

CONCLUSIONS

The graft polymerization of **I** to PA-6 thread with **II** included the homolytical substitution of hydrogen atoms in α-CH_2— groups of —HN—CH_2—$(CH_2)_4$—C(O)— chains and led to the creation of ester polyfluorinated alkyl groups on the end of polyamide macromolecules that increased the tensile strength of the PA-6 thread.

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