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Polyfluoroalkoxyethylperoxydicarbonates as efficient initiators of fluoro-olefin polymerization (copolymerization)

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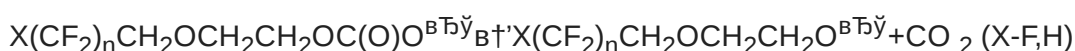
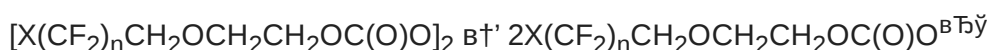
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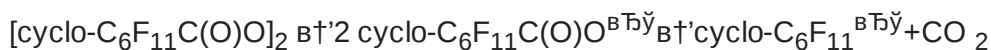
Abstract: Initiators of formula $X(\text{CF}_2)_n\text{CH}_2\text{OCH}_2\text{CH}_2\text{OC}(\text{O})\text{O}]_2$ (here X - F, H) increase thermal resistance and improve properties of polyvinyl-, vinylidene fluorides, and tetrafluoroethylene-hexafluoropropylene co-polymer.

Key words: Vinyl, vinylidene fluoride, poly(vinyl, vinylidene)fluorides, co-polymer of tetrafluoroethylene and hexafluoropropylene, polyfluoroalkoxyethylperoxydicarbonate.

Recently some researchers [1-8] considered the impact of polyfluorinated substituents on physico-chemical properties and initiating activity of peroxides. In one report [9] they discussed the impact of dimethylene oxide group in peroxides on their stability. Thus, no decomposition of peroxide $[\text{H}(\text{CF}_2\text{CF}_2)_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OC}(\text{O})\text{O}]_2$ was observed after 180x24 hours storage at 5B°C, while its half-life was 7.7 hours when heated in benzene at 50B°C. The peroxide thermolysis follows the reactions:



It is also well known that thermolysis of perfluoroacylperoxides results in the formation of perfluoro-oxacyl and perfluoro-alkyl radicals [6]. Thus thermolysis of perfluorocyclohexanoyl peroxide (PFCP) results in perfluorocyclohexanoyl and perfluorocyclohexyl radicals:



Here we compare the process parameters for polymerization of vinyl-, vinylidene- fluorides, copolymerization of tetrafluoro- ethylene with hexafluoropropylene at the conditions of various poly- or perfluorinated radicals $\text{B}\ddot{\text{T}}\ddot{\text{y}}^{\text{TM}}$ formation. The rate of polymerization, i.e. amount of product per time unit, and thus formed polymer properties are shown in a Table 1.

Table 1. Process parameters and properties of fluoropolymers produced in the presence of fluorinated initiators.

From the table one may see that fluoropolymers produced in the presence of polyfluoro-alkoxyethyl peroxydicarbonates exhibit higher thermal stability than those produced in the presence of PFCP initiator that manifests in lower polymer mass loss at high temperature. This, further, contributes to considerable (two-threefold) expansion of temperature interval of fluoropolymer processing to marketable articles. The said interval is the difference between the minimal temperature of bubble nucleation in melt and that of polymer molding. The expansion of temperature interval for polymer

processing is especially important for polyvinylfluoride as its flow melt temperature is usually close to that of its thermal decomposition.

The ultimate tensile strength of polyvinylfluoride produced with 2-(tetrafluoropropoxy) ethoxy-percarbonate is 52 MPa, while that of produced with PFCP is only 40 MPa. With comparatively small difference in polymerization temperature the polymerization rate is nearly three times higher, and percentage elongation is 120% (with PFCP it is 60%). It is possible that high elasticity is due to the presence of $\text{H}(\text{CF}_2\text{CF}_2)_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}$ вЂ“fragment introduced into polyvinylfluoride structure.

The comparison of polymerization rates of vinylidene fluoride using differently structured initiators has shown that with 2-(tetrafluoropropoxy) ethoxy-percarbonate the rate of polymerization is 5 times higher (temperature 45B°C), and when heated to 275B°C during 5 hours the mass loss of resulting polymer is much less.

Copolymerization of tetrafluoropropylene with hexafluoropropylene was conducted at 50-60B°C. The stability of co-polymer produced with 2-(dihydroperfluoroheptoxy) ethoxy percarbonate exceeds that of co-polymer produced with PFCP at 300B°C during 5 hours. What also stands out is considerable decrease in number of pectous inclusions in tetrafluoroethylene/ hexafluoropropylene co-polymer (0-3 inclusions sized 0.2-0.5mcm, and 0-1.8 inclusions sized 0.5-1mcm), that is much less than with PFCP. Therefore, it allows considerable improvement of the article quality and decreasing of flaw.

Therefore, polyfluoroalkoxyethyl peroxydicarbonates may be recommended for efficient initiators in the polymerization of vinyl fluoride, vinylidene fluoride, and in the copolymerization of tetrafluoroethylene with hexafluoropropylene in order to improve the performance of articles produced of them.

Experimental

Polymerization of vinylfluoride

A 1l stainless steel autoclave, preliminary flushed with oxygen-free inert gas, is charged with 100ml of water; 0.5g of di-2-(1,1,3-trihydrotetrafluoropropoxyethyl)peroxydicarbonate, 100ml of freon-113. The autoclave is cooled to minus 60B°C, evacuated and 120g of vinylfluoride (VF) is added. The autoclave is sealed at continuous shaking, heated at 60B°C during 9 hours (initial pressure was 35 atm). Then the autoclave is cooled, surplus monomer is withdrawn by inert gas, polymer is separated, washed and dried at 80-90B°C to permanent mass. The yield is 90g.

Polymerization of vinylidene fluoride

The autoclave is charged with 500ml of salt-free water, 1.0g of di-2-(1,1,5-trihydrooctafluoropentoxyethyl)peroxydicarbonate (0.6% of the monomer mass). The autoclave is closed, pre-treated as described above, and charged with 50g of vinylidene fluoride (VDF); when so doing the autoclave is heated to 70B°C, and the maximal pressure is 30 atm. The process total duration is 2.5 hours. It results in water dispersion with the solid content 20.6 %. The finish product yield is 130g. The properties of resulting (co)polymers are shown in table below.

Copolymerization of tetrafluoropropylene with hexafluoropropylene

Copolymerization was conducted according to the procedure described in a patent [10]. PFCP (reference initiator) is synthesized following the procedure from fluoroanhydride of perfluorocyclohexane acid and aqueous hydrogen peroxide mixed with 17% (by mass) water solution of sodium hydroxide and an organic solvent вЂ“perfluoromethylcyclohexane (Freon 350) at minus 10 to minus 15B°C. Both polymerization and co-polymer isolation are conducted according to the patent [10].

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Recommended for publication by Prof. A.I. Rahimov