

**Synthesis and application  $\alpha$ -bromo-perfluoroalkylvinyl ethers.**

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**Report VI. Study of some conditions of processing copolymers of fluoroolefins with  $\alpha$ -bromo-perfluoroalkyl ethers.**

**Introduction**

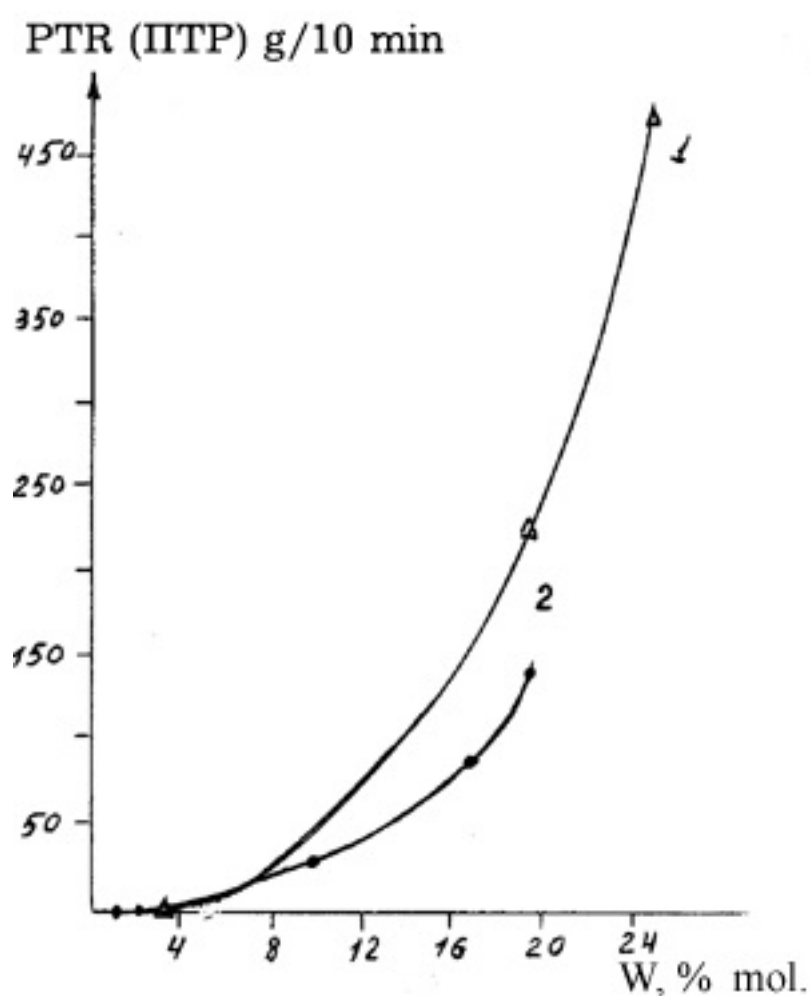
During the investigation of the conditions of copolymerization of tetrafluoroethylene (TFE) and vinylidene fluoride (VDF) with  $\alpha$ -bromo-perfluoroalkylvinyl ethers (BrAVE) and also during the study of their physical and mechanical properties, a significant heterogeneity of their properties in comparison with other fluoropolymers based on TFE and VDF has been found. Considerable data scattering of the properties of different lots of the copolymers produced under identical conditions and having close molecular mass and ratio of TFE (VDF):BrAVE was observed.

Therefore, some investigations on determination of the process conditions for processing copolymers to stabilize the properties of articles made from them were carried out.

**Determination of flow and fusibility of the copolymers of BrAVE with TFE and VDF.**

The melt flow index was taken as the main characteristic of the new fluoropolymers. It was determined on a capillary plastometer IIRT-M according to State Standard 11645-13. The load was 2.16 kg, draw plate diameter of 2.093mm, 270°C.

The data of fluidity of copolymers of TFE with BrAVE are given in Fig.1 ( Curve 1: BrAVE-2; curve 2: BrAVE-4)



**Fig.1.** Dependence of the melt flow index of copolymers of TFE with BrAVE on the BrAVE monomer content ( $W$ , mol%) and its chain length.

As it is seen from Fig.1, flow of the melts of copolymers of TFE with BrAVE is slightly decreasing with the growth of the chain length in the alkyl fragment of the BrAVE monomer and sharply increasing with the increase of the BrAVE content in the copolymer; the flow increase is observed from the BrAVE content of approximately 3mol %.

As it should be expected, the behavior of TFE copolymers with divinyl ethers produced from BrAVE monomers according to the scheme described in report IV is absolutely different.

The introduction of less 0.1mol% of diene into the chain of TFE copolymer with perfluorobutylvinyl ether (DVE-4) almost does not affect the copolymer properties; when the quantity is increased to 0.2-0.3%, the melt flow index is reduced approximately twice. A further heat processing of the polymer does not change the melt flow index. The introduction of 0.5-1 mol% of DVE-4 to the chain results in a polymer with a very low melt flow index (0.1-0.5g/10min) and its pressure molding into film leads to an additional cross-linking with complete flow loss.

Copolymers of DVE-4 with VDF containing 1-1.3mol.% of diene are high-melting soluble products difficult to process into a film but after heat treatment (200-250°C) during pressing they lose their flow and solubility that is confirmed by the data of IR-, F NMR-spectroscopy.

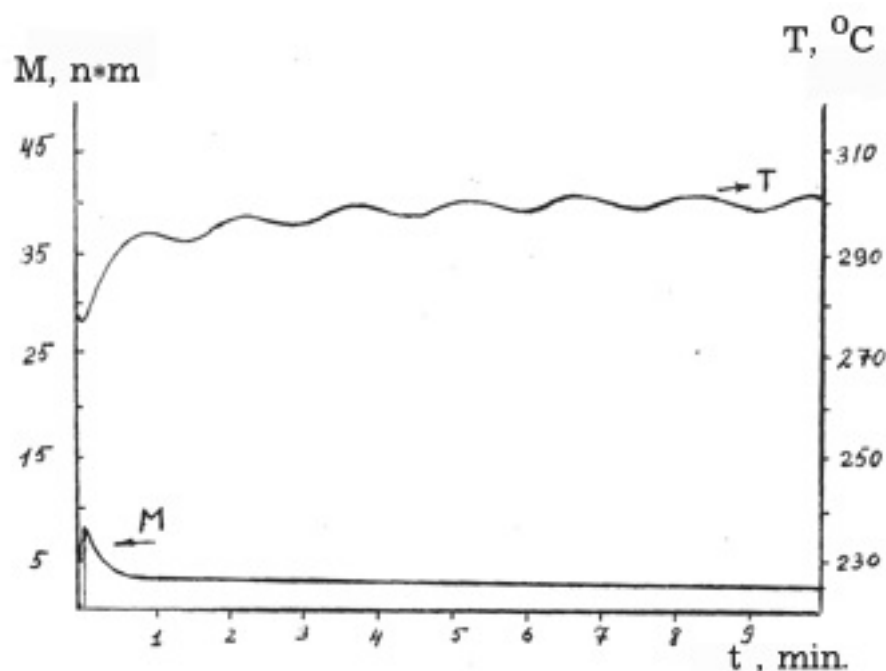
### **Homogenization of BrAVE copolymers with fluoroolefins.**

Both in determination of physical and mechanical properties of BrAVE copolymers with TFE and VDF, and in determination of the melt flow indices, considerable discrepancies in data on copolymers of identical compositions have been noted. Therefore homogenization of the polymer by additional stirring of its melt was used as a processing route to stabilize characteristics of films and other articles made from new fluoropolymers. The homogenization was carried out on a laboratory rheological measuring device, "Plasticorder PLD-331" of "Brabender" (Germany) made with the use of a mixer of W 50H type.

The duration of mixing was 10 minutes at a temperature of 277-300°C and at a speed of

rotation of operating elements of the mixer of 70 rpm.

The homogenization process was controlled by values of the torque on the drive axis of the mixer  $M$ , nm, and by the temperature of copolymer melt  $T$ , °C, in the mixer chamber. These data as dependencies  $M=f(t)$  and  $T=f(t)$ , where  $t$ , min, is the time from the moment of sample loading into the mixer, are given in Fig.2 for the copolymer sample containing 3 mol.% of BrAVE ( MFI=1.45 g/10min at 270°C and elevated load  $P=10$ kg).



**Fig.2** Dependence of torque  $M$ , nm, and melt temperature  $T$ , °C, on the homogenization time

It is seen that at the moment of loading a powder sample, the  $M$  value is the maximal and further it is decreasing with the copolymer melting. During the subsequent homogenization the  $M$  value is monotonously reducing with increase in  $t$  value that may be explained by processes of thermal and mechanical destruction of the sample. But the value of this reduction during 10 minutes of the homogenization ( that corresponds to the real residence time for the copolymer melt in the processing equipment) is small.

As another example, a copolymer sample containing 4.5 mol% of BrAVE had melt flow index of 0.16g/10min prior to homogenization. After the homogenization, the value of melt flow index increased to 43.6 g/10min. Redefinition of the melt flow index for the same sample gave the value of 58g/10min, later on the value of melt flow index remained the same.

The given data are the evidence of the good result of the homogenization of BrAVE copolymers with fluoromonomers, namely: the flow index of the copolymer is stabilized that allows to process it with conventional methods and multiple granulation does not worsen the melt properties but also is necessary before processing into articles.

### **Development of regimes of compression pressing of BrAVE copolymers with TFE and VDF.**

As it was noted, the modification of polytetrafluoroethylene by perfluoromonomers with functional groups gives fluidity and availability for its processing by conventional for plastics methods .

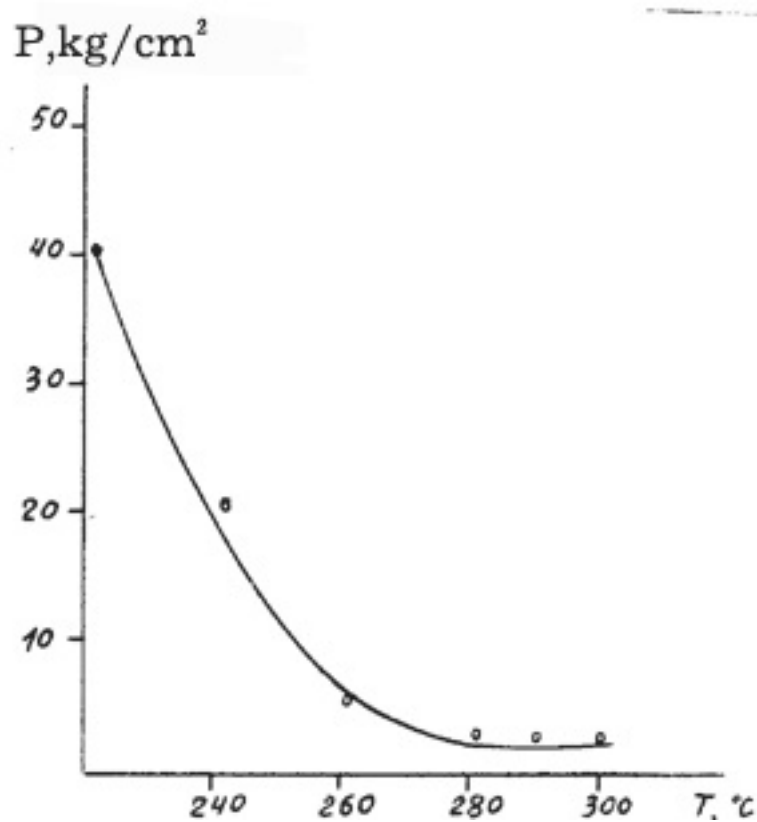
Development of regimes of compression pressing films from the copolymers produced was carried out on a K-18 press (Poland). The sizes of films manufactured were (0.17-0.025) mm at the following parameters: load mass of 6g, electrical heating power of 2800W, mold mass of 13.7 kg.

Copolymers containing 1.3-19.5mole % of bromine-containing polymer were studied. The

pressing conditions varied within a wide range: temperature of 220-350°C, specific pressure of 5-140 kgf/cm. The quality of films was evaluated visually (transparency, absence of bubbles, of foreign inclusions and gels), according to polythickness (a Micrometer) and brittleness (a NG-1 instrument). Satisfactory quality of the films was attained using copolymers of TFE with 3-19.5% (mole) of bromoperfluoroethylvinyl ether.

When the BrAVE content is reduced to 1.3 mol % at a pressing temperature of 310°C and pressure of 12 kgf/cm, a brittle film is formed obviously due to insufficient material melting. Only at a temperature of 340-350°C and pressure of 80-100kgf/cm some increase in elasticity and transparency of the films is observed.

The optimal regimes of pressing films of TFE copolymer with 10% (mole) BrAVE are given in Fig.3 as pressure versus temperature providing fabricating high-quality films. Average rates of heating and cooling the mold were 6 and 7.5 °C/s respectively.



**Fig.3** Optimal conditions ( pressure,  $P$ ,kgf/cm and temperature,  $T$ ,C) for pressing films from the copolymer of TFE and BrAVE (10mole %)

## Conclusions

The influence on the fluidity of melts of copolymers of TFE and VDF with BrAVE of the content and chain length of BrAVE monomer in the fluoroalkyl fragment of the copolymer molecule has been studied.

It has been found that the fluoropolymers produced can be processed by conventional methods and the method to stabilize the properties of the copolymers by homogenization has been developed.

The optimal regimes of compression pressing of the films from the copolymers produced has been developed.