

This article was downloaded by:

On: 19 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

### Reactivity of Perfluoralkyl(meth)acrylates in Radical Copolymerization with Some Vinylcontaining Monomers and Properties of Their Co-polymers

N. G. Lekishvili<sup>a</sup>; L. P. Asatiani<sup>a</sup>; T. T. Guliashvili<sup>a</sup>; L. M. Khananashvili<sup>a</sup>

<sup>a</sup> Chemical Department, Tbilisi State University, Tbilisi, Republic of Georgia, C.I.S.

**To cite this Article** Lekishvili, N. G. , Asatiani, L. P. , Guliashvili, T. T. and Khananashvili, L. M.(1995) 'Reactivity of Perfluoralkyl(meth)acrylates in Radical Copolymerization with Some Vinylcontaining Monomers and Properties of Their Co-polymers', *International Journal of Polymeric Materials*, 27: 3, 163 – 174

**To link to this Article:** DOI: 10.1080/00914039508009667

**URL:** <http://dx.doi.org/10.1080/00914039508009667>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# Reactivity of Perfluoroalkyl(meth)acrylates in Radical Copolymerization with Some Vinylcontaining Monomers and Properties of Their Co-polymers

N. G. LEKISHVILI, L. P. ASATIANI, T. T. GULIASHVILI and L. M. KHANANASHVILI

*Chemical Department, Tbilisi State University, 3, Chavchavadze Ave., Tbilisi, 380028, Republic of Georgia, C.I.S.*

*(Received March 9, 1994)*

The reactions of co-polymerization of perfluoroalkyl(meth)acrylates ( $n,F(M)A$ ) with MMA, styrene and dimethylvinylethynylcarbynol (DVEC) in mass, in benzoyl peroxid (BPO) presence are studied using GLC, NMR- $H'$  spectroscopy high resolution, UV- and IR-spectroscopy and dilatometry. Constants of copolymerization  $r_{ij}$  and  $r_{ji}$ , distribution of homo- and heterodiads in macromolecular chain and copolymerization speed are determined using data of composition of co-polymers. Quantum chemical parameters of vinyl groups of perfluoroalkyl(meth)acrylates in radical co-polymerization with the above-mentioned monomers on the basis of received results is determined. The optical, thermomechanical properties and thermo-oxygenational stability of the obtained co-polymers are studied. The dependence of these properties on structure of  $n,F(M)A$  and their molar ratio in the reaction mixture and conditions of reactions are established.

**KEY WORDS** Fluoroalkyl(meth)acrylates, reactivity, co-polymerization, thermostability, optical transparent.

## INTRODUCTION

The co-polymers based on fluorine containing (meth)acrylates attract wide attention among scientists who attempt to develop the optical transparent medium with the high reflection of light.<sup>1-3</sup>

The design of these polymers with the good optical and physical-mechanical indexes is directly related to the structure of their macromolecular chain. But there has been only data on the effect of the macromolecular chain structure of the co-polymers and reactivity of fluoro(meth)acrylates, as well as on the quantitative description of their co-polymerization with the other vinylcontaining monomers. To a degree this discourages the development of a theoretical model that would facilitate the search for polymeric reflective layers with the good optical properties.

Therefore, the present work is dedicated to the study of the relative reactivity of some perfluoroalkyl(meth)acrylates in the radical co-polymerization with MMA,

styrene (St) and dimethylvinylethynylcarbynol (DVEC), as well as the structure of macromolecular chain, optical and thermomechanical properties and thermostability of these co-polymers.

## EXPERIMENT, RESULTS AND DISCUSSION

As perfluoroalkyl(meth)acrylates, we selected 1,1,5-trihydrooctafluoroamylmethacrylate ( $M_2$ ), 1,1,3-trihydrotetra fluoropropylmethacrylate ( $M_3$ ) and -acrylate ( $M_4$ ), also 1,1,1-trifluoroethylmethacrylate ( $M_5$ ), obtained by the methods described in Reference 4. For co-polymerization we used the monomers containing not less than 99,7 mass% of the essential substance. MMA( $M_1$ ), styrene ( $M_6$ ) and DVEC ( $M_7$ ) were rectified by the standard methods.<sup>6</sup> We controlled the purity of monomers by the methods of glass-liquid chromatography (GLC), "Chrom," DIP, Sorbent PPGA (15%) on the chromatone AW, dissolvent dimethylformamide (DMFA)<sup>5</sup>. As an initiator, we used twice recrystallized from methanol BPO (0,001 mole per 1 mole of the monomers mixture) containing more than 99,6 mass - p.c. of the essential substance.

The co-polymerization was carried out in bulk (348K) up to a conversion not exceeding 10 mass%, proceeded by the degassation using the highvacuum recondensation method (AV-65). The obtained co-polymers were purified using two-way reprecipitation with hexane from the diluted solutions in acetone. We determined the polymerization speed by the dilatometry method (molybden glass, volume 5.0 ml,  $dm \sim 1$  mm). We controlled the change of the reaction mixture volume with the cathetometer to within 0.02 mm.

The composition of co-polymers ( $m_{i,j}$ ) and the reaction mixture was determined using <sup>1</sup>H-NMR<sup>8</sup> ("Tesla", 80 MHz TMS,  $CDCl_3$ , 298K), GLC and the elemental analysis in co-polymers.

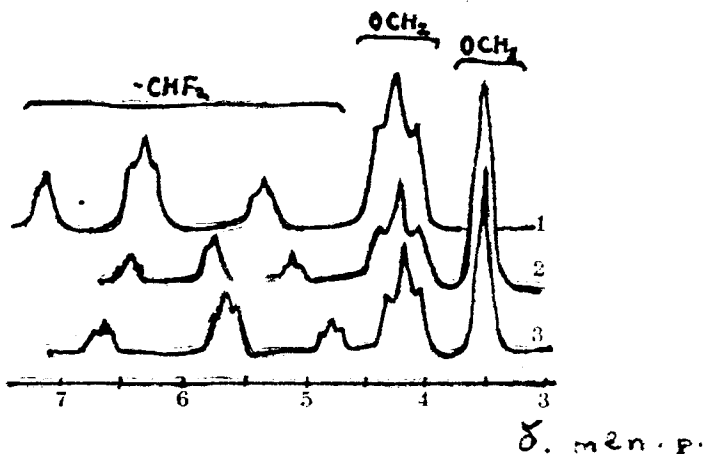


FIGURE 1 <sup>1</sup>H-NMR-spectra of the fluorine-containing co-polymers: 1.-poly- $M_3$ , 2.-co-polymer  $M_1-M_3$ , 3.-co-polymer  $M_1-M_3$ .

We used the signals of protons in the  $-\text{CH}_2\text{F}_2$  and  $\text{CHF}_2$  groups ( $7.5-5.0\sigma$ ) (Figure 1) to determine the composition of co-polymers by the  $^1\text{H-NMR}$  method.

Quantities of  $m_i$ , established using  $^1\text{H-NMR}$  spectra, were compared with the composition data, computed from the reaction mixture analysis by the GLC and elem. anal. methods (%F). This showed a good agreement between the results of  $^1\text{H-NMR}$  and GLC methods (Figure 2, Table I).<sup>3</sup>

Using the data of the co-polymers composition and assuming that the reactions of increasing of chain are described with the classical Kelen-Tudos method, the constants of co-polymerization  $r_{ij}$  and  $r_{ji}$  are computed.<sup>7</sup> The following results were obtained for the system  $n_1\text{FMA}$  with  $\text{MMA}$ , and  $n_1\text{FMA}-n_1\text{FA}$ :  $M_1-M_2$ ,  $r_{12} = 0,59$ ,  $r_{21} = 0,72$ ,  $M_1-M_3$ ,  $r_{13} = 0,85$ ,  $r_{31} = 0,80$ ,  $M_1-M_4$ ,  $r_{41} = 0,23$ ,  $M_3-M_4$ ,  $r_{54} = 3,22$ ,  $r_{43} = 0,9$ ,  $M_1-M_5$ ,  $r_{15} = 0,74$ ,  $r_{51} = 0,78$ .

The dependence of the co-polymer's composition ( $M_i$ ) on the content of mon-

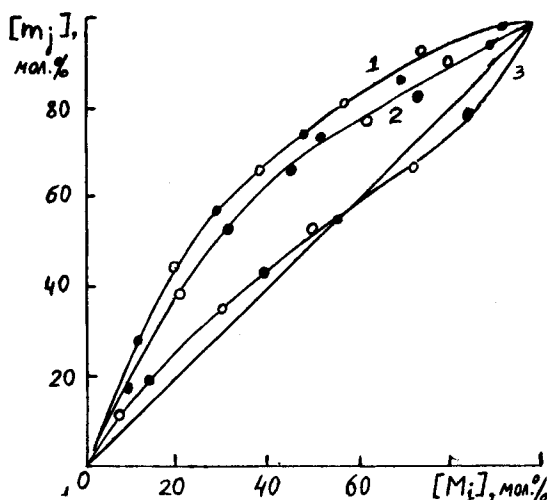


FIGURE 2 The dependence of the co-polymer's composition on the composition of the initial monomers medley in the systems: 1.- $M_1-M_4$ , 2.- $M_3-M_4$ , 3.- $M_1-M_3$  (o-GLC,  $^1\text{H-NMR}$ ).

TABLE I

The dependence of the co-polymers composition and ratio of the homo- and heterodiades on the initial  $M_1-M_2$  monomers mixture composition

The composition of the initial mixture, %		Co-polymers, composition, mol. %				The diades ratio	
		$^1\text{H-NMR}$		GLC			
$M_1$	$M_2$	$m_1$	$m_2$	$m_1$	$m_2$	$M_1M_1$	$2 M_1M_2$
18,0	82,0	22,0	78,0	21,5	78,5	0,03	0,38
25,0	75,0	27,5	72,5	28,0	72,0	0,05	0,50
42,0	58,0	41,0	59,0	40,6	59,4	0,12	0,65
48,0	52,0	44,2	55,8	45,5	54,5	0,14	0,64
61,0	39,0	57,0	43,0	58,0	42,0	0,25	0,63
75,0	25,0	70,5	29,5	69,0	31,0	0,41	0,54
80,5	19,5	75,5	24,5	74,5	25,5	0,62	0,25

omers ( $M_i$ ) in the initial mixture for the  $M_1$ - $M_2$  and  $M_1$ - $M_3$  systems (Figure 2, Table I) confirms the often-observed case where both constants  $r_{ij}$  and  $r_{ji}$  are less than unit. In this case, the composition's curve (Figure 2, curve 3) crosses the line, going at an angle of  $45^\circ$ , the crossing point agrees with the composition of the monomers mixture, when the polymer of the same composition is created (azeotropical point). Using the formula  $M = 1 - r_{ii}/2 - r_{ij} - r_{ji}$ , the azeotropical compositions of the initial monomers mixture are calculated, with the following results: for  $M_1$ - $M_2$  this correlation is 40,6:59,4 mol.%, for  $M_1$ - $M_3$ , 57,1:42,9 mol. %.

The experiment confirmed the validity of these data (Figure 2, Table I). For the systems  $M_1$ - $M_4$  and  $M_3$ - $M_4$  the present co-polymer is enriched with the links of more active component  $M_1$  and  $M_3$  (Fig. 2, curves 1,2) in the entire range of the initial ratio of monomers.

It shows the tendency of the systems  $M_1$ - $M_2$  and  $M_1$ - $M_3$  to interchange the links in the macromolecular chain, as radicals  $M_1$ ,  $M_2$  and  $M_3$  more preferably take part in the reactions. As a result, the content of heterodiades in the macromolecular chain increases and its final ratio exceeds 0,5 where  $M_1$  in the initial mixture falls in the 30-60 mol. % interval.

The analysis of the distribution of diades hetero- and homodiades ( $M_1$ - $M_4$  and  $M_3$ - $M_4$  diades) (Figure 3) indicates the increasing content of homodiades of these co-polymers with increasing monomer ratio.

The change of rate, for the systems  $M_1$ - $M_2$  and  $M_1$ - $M_3$  (Figure 4, curves 1, 2) is linear almost in the range of the studied composition, but it has an extreme point in presence of  $M_4$ , 30-40 mol. % and  $M_3$ , 45-50 mol. % in the initial mixture for the systems  $M_1$ - $M_4$ ,  $M_3$ - $M_4$ . The curves 3, 4 (Figure 4, systems  $M_2$ - $M_4$ ,  $M_3$ - $M_4$ ) are characteristic of the case, when  $r_{ij} < 1$  and  $r_{ji} > 1$ .

As expected the values of the co-polymerization rate for the systems  $M_1$ - $M_2$ ,  $M_1$ - $M_3$  are higher than, for example, the system  $M_1$ - $M_4$ .

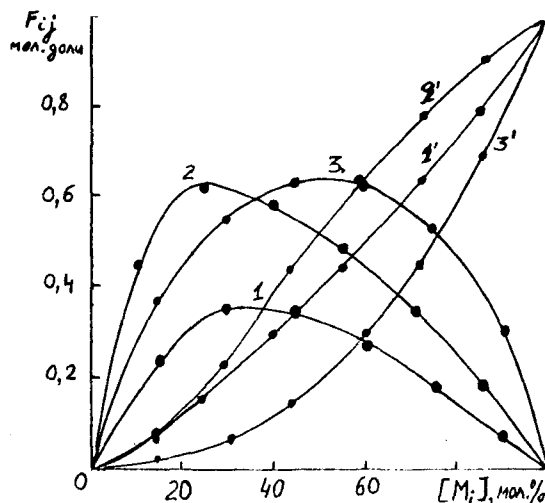


FIGURE 3 The dependence of the hetero-(1,2,3) and homodiades (1',2',3') ratio on the composition of the initial monomers in the systems: 1.- $M_2$ - $M_4$ , 2.- $M_3$ - $M_4$ , 3.- $M_4$ - $M_5$ .

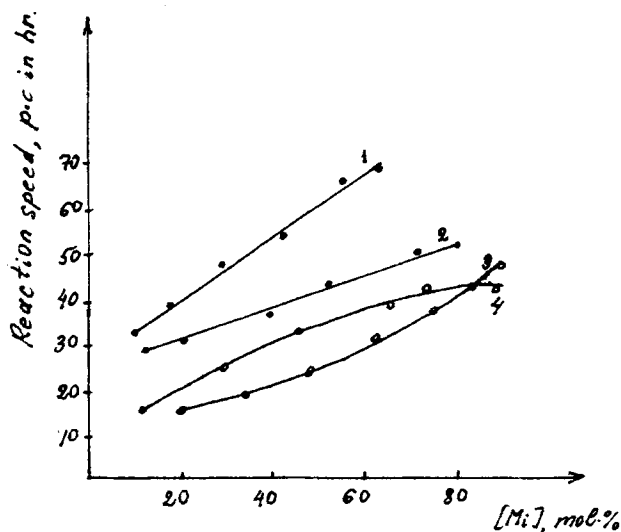


FIGURE 4 The dependence of the co-polymerization rate of the co-polymer (% in hour) on the composition of the monomers initial medley ( $M_1$ -4FMA, 8FMA): 1.- $M_1$ - $M_3$ , 2.- $M_1$ - $M_2$ , 3.- $M_3$ - $M_4$ , 4.- $M_1$ - $M_4$ .

TABLE II

Some quantum-chemical parameters of the perfluoroalkyl(meth)acrilates and MMA

Monomer	$q^a$	$q^b$	$(\Sigma q)C_\alpha H_2$	$P_{C=C}^\pi$	$P_{C=C}^{full}$	$E_{HSMO}$ , e.v.	$E_{LSMO}$ , e.v.	$E_{full}$ , e.v.
MMA	-0,125	+0,062	+0,121	0,9455	1,8461	-10,1747	+0,4579	-1374,75
3FMA	-0,121	+0,052	+0,113	0,9462	1,8512	-10,5557	-1,2796	-2922,03
4FMA	-0,120	+0,050	+0,101	0,9501	1,8660	-9,5259	-1,5622	-3540,24
4FA	-0,129	+0,071	+0,125	0,9695	1,8901	-9,2400	-1,3307	-3383,68

The above experimental data are in agreement with the quantum chemical calculations of perfluoroalkyl(meth)acrylates (Table II). The quantum chemical calculations were carried out using the MINDO 3 method to obtain the standard Dewar parameters.<sup>8</sup> The spatial structure and charges on the atoms are shown in Figure 5. For comparison we show the corresponding data of methylmethacrylate unleashes in Table II, Figure 5.

Because the essential reaction centers of perfluoroalkyl(meth)acrylates are the vinyl groups, the authors of the present work focus on the parameters of this group with the different substituents at the  $\alpha$ -carbon (H,  $CH_3$ ). The essential quantum chemical parameters of the above-mentioned monomers are listed in Table II. As evidenced by Table II, comparing with 4FA( $M_4$ ), for the homologue monomers MMA, 3FMA and 4FMA (with the methyl substituents at the  $\alpha$ -carbon of the vinyl group) the important development in the electrical structure and parameters of double bond of vinyl group is observed, effecting to some degree its strength ( $P_{C=C}^\pi$ ,  $P_{C=C}^{full}$ ) and consequently, the reactivity of the monomers.<sup>9</sup>

We also used the well-known scheme of  $Q-e$  Alfrey-Price<sup>10</sup> to confirm the ex-

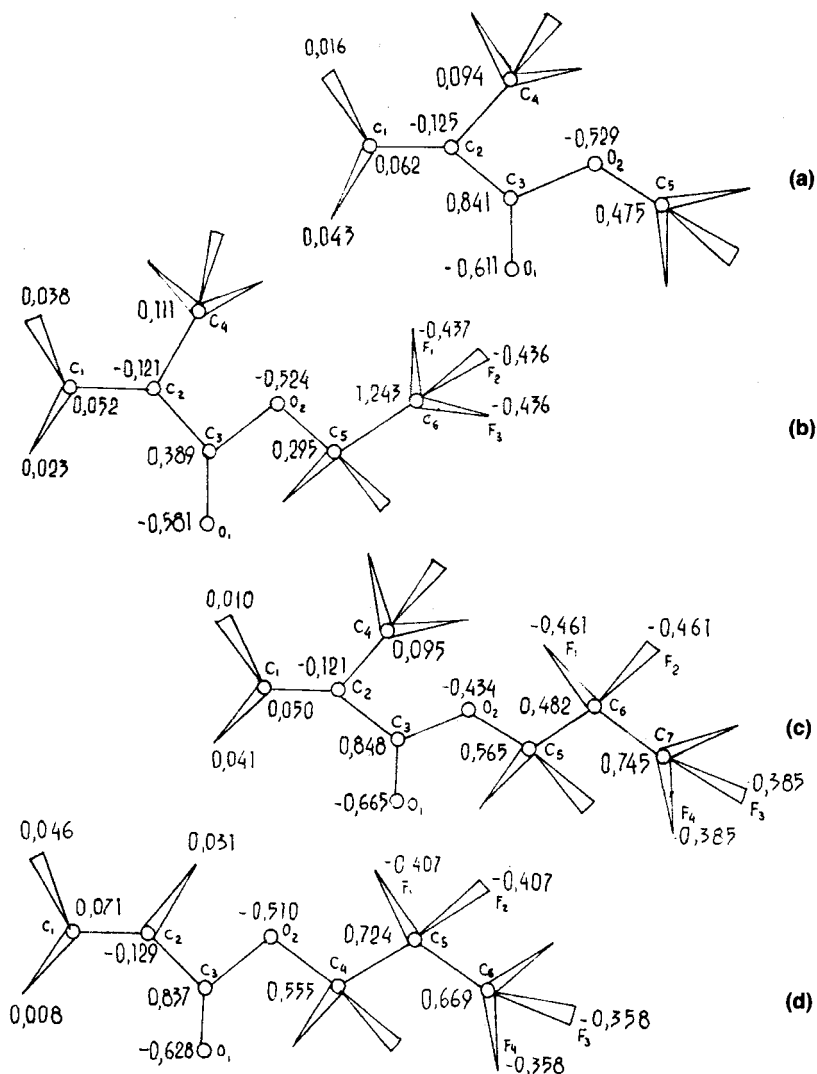


FIGURE 5. The spatial structure and the charges on the atoms of the molecules MMA(a), 3FMA(b), 4FMA(c) and 4FMA(d).

TABLE III

Comparison of the calculated quantum-chemical data with some experimental parameters of  $n,F(M)A$  in co-polymerization with MMA

Monomer	$q^B$	$P_{C=C}^{full}$	$P_{C=C}^{\pi}$	$1/r_v$	$Q_i$
3FMA	0,052	1,8525	0,9462	1,282	0,75
4FMA	0,050	1,8713	0,9501	1,250	0,60
4FA	0,071	1,8955	0,9695	0,649	0,34

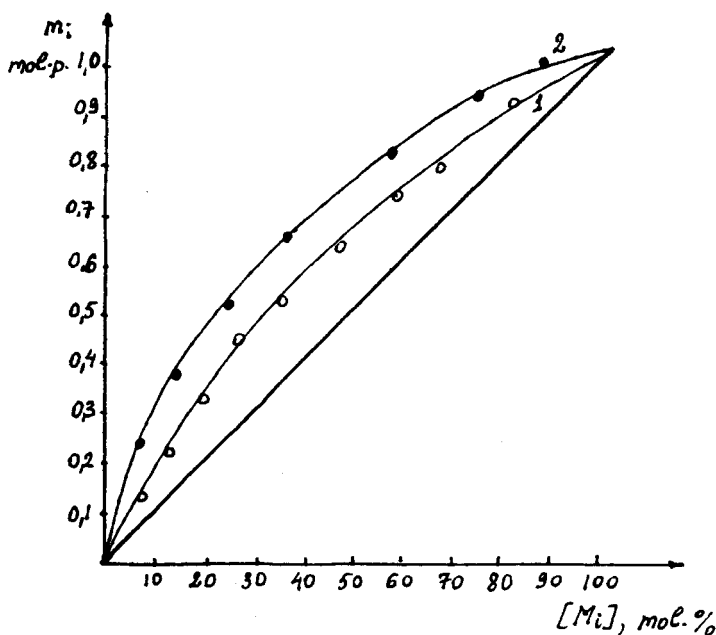


FIGURE 6 The curves of  $m_1 = f(M_1)$  dependence for the systems: 1.-4FMA-DVEC, 2.-8FMA-DVEC.

perimental and theoretical data about the relative reactivity of perfluoroalkyl(meth)acrylates. Comparing  $q^B$ ,  $P_{C=C}^{\pi}$ ,  $P_{C=C}^{\text{full}}$  (double bond) with the parameters  $1/r_2$  and  $Q_i$  despite the relatively small quantity of fluorine containing monomers used in the research, a definite correlation is observed (Table III).

In case of co-polymerization of  $n_1$ FMA (4FMA) with styrene, the meaning of  $r_{36} = 0,61$  and  $r_{63} = 0,49$  are also confirmed by the tendency of the above-mentioned co-polymers to interchange the monomeric links. At the co-polymerization of  $n_1$ FMA (4FMA and 8FMA) with DVEC there is observed the different trend namely the fluorine-containing monomers react more energetically with theirs than with "another's" radicals ( $r_{37} = 1,75$ ,  $r_{73} = 0,55$ ,  $r_{27} = 1,43$ ,  $r_{72} = 1,21$ ). As evident from Figure 6, practically in the entire range of the initial ratios of the monomeric mixture of the systems  $n_1$ FMA- $n_1$ FA, the resulting co-polymer is enriched with the links of the more active component  $n_1$ FMA.<sup>11</sup> The structures and compositions of the obtained co-polymers  $n_1$ FMA-DVEC were established using IR, UV, 'H-NMR-spectra and the element analysis data. There are detected absorption maxima in the region of  $1600 \text{ cm}^{-1}$ ,  $3100 \text{ cm}^{-1}$ ,  $1720\text{--}1750 \text{ cm}^{-1}$ ,  $1070\text{--}1250 \text{ cm}^{-1}$ ,  $2900 \text{ cm}^{-1}$ ,  $3400\text{--}3600 \text{ cm}^{-1}$ , corresponding to the asymmetric oscillation of  $>C=C<$ ,  $=CH$ ,  $>C=O$ ,  $-C(O)-O-$ ,  $CF_2-$ ,  $CHF_2-$ ,  $CH_3-$ ,  $OH-$  groups. The weak absorption maxima are also found in the region of  $2150 \text{ cm}^{-1}$ , which corresponds to the substituted asymmetric  $-C\equiv C-$  bonds.<sup>12</sup> This is confirmed, for example by the presence of  $\lambda = 1,95 \text{ nm}$  in UV-spectra of co-polymers, which contain the asymmetric alkyne compounds. In the 'H-NMR spectra we detected the signals at  $4,5$  and  $6,0\sigma$ . Therefore, we concluded that the macromolecular chains of the present co-polymers contain the acetylenic fragments in the side chain.<sup>11</sup>



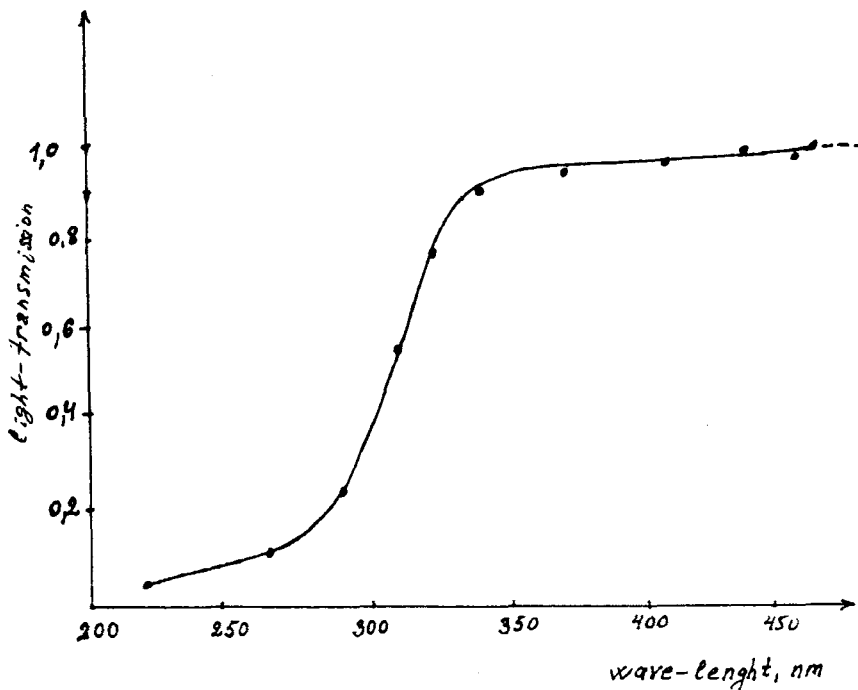


FIGURE 7 Light-transmission of co-polymer 8FMA-DVEC (10:90 mass%).

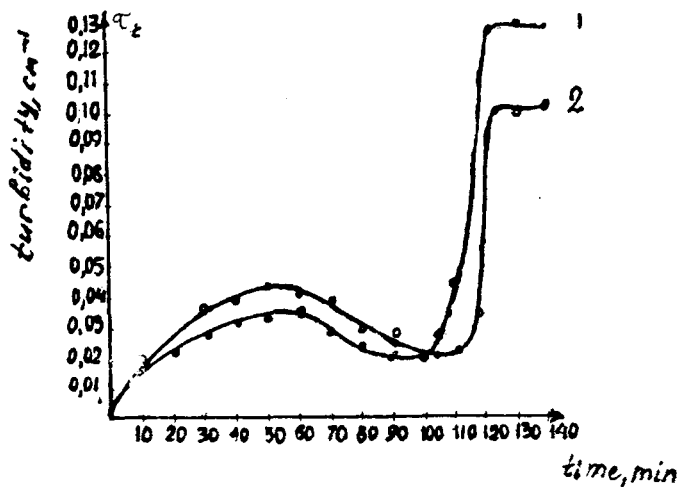


FIGURE 8 The dependence of turbidity ( $\lambda = 350$  nm) on the co-polymerization time (for azeotropic mixture of 4FMA-MMA).

The obtained co-polymers are solid transparent products. They are soluble in acetone, DMFA, ethylacetate etc. After evaporation of the solvents, they form on the glass or metallic surfaces transparent films, with a quite good transmission of light in the visible region (350–800 nm) (Figure 7). They have a good adhesion to

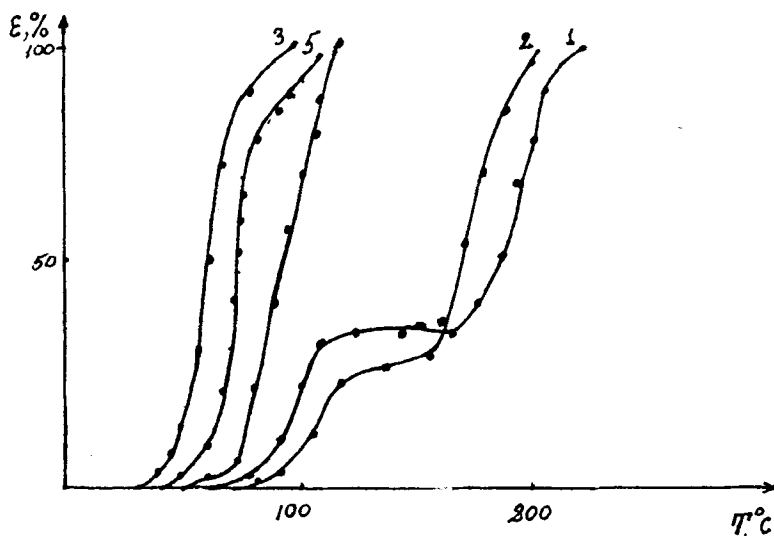


FIGURE 9 Thermomechanical curves for co-polymers: 1.-8FMA-MMA (59,4:40,6 mol.%), 2.-4FMA-MMA (42,9:57,1 mol.%), 3.-4FMA-DVEC (90:10 mass%), 4.-8FMA-DVEC (90:10 mass%), 5.-8FMA-DVEC (70:30 mass%).

the organic polymers (PMMA, PVA and the others) and the glass and are hardenable by chemical or photochemical methods.

The optical and thermomechanical properties and thermo-oxidative stability of these co-polymers were also studied.

The optical properties were studied using spectrophotometer "Specol", in the following wavelength region: 350–550 nm. We investigated 4FMA-MMA and 4FMA-St. The study was carried out during the process of the co-polymerization in a special glass container with the following dimensions: 25,0 × 25,0 × 10,0 mm. The temperature was  $T = 343\text{--}353\text{K}$ .

The obtained spectrograms were worked up using the method of "Spectra turbidity."<sup>13</sup> Investigating the optical properties of co-polymer 4FMA-MMA (azeotropic mixture), which is characterized by the turbidity meaning ( $\tau_t$ ), its dependence on the reaction temperature and the reaction time was found (Figure 8). On the deepest stage of the co-polymerization (conversion 95%) a noticeable change in the system's optical properties takes place. The change is appreciable for the system 8FMA-St. A temperature increase up to 363K promotes the creation of more transparent co-polymer ( $\tau_t \sim 0,57 \text{ cm}^{-1}$  for 10 mass% of St).

The investigation of thermomechanical properties for co-polymers  $n_i\text{F(M)A-MMA}$ ,  $n_i\text{F(M)A-DVEC}$  (heating speed 1°/min) demonstrates that  $T^g$  of co-polymer, generally, depends on the co-monomer's structure. Particularly, in case of 4FMA:MMA and 8FMA:MMA, co-polymers have small sections of highelasticity, which indicates at their relatively low molecular masses (Figure 9, curves 1, 2).  $T^g > 80\text{--}90^\circ\text{C}$ , co-polymers  $n_i\text{FMA-DVEC}$  have thermomechanical curves, peculiar to low-molecular thermoplastic polymers with  $T^g > 50\text{--}85^\circ\text{C}$ , depended on the  $n_i\text{FMA}$  structure and molar ratio of  $n_i\text{FMA-DVEC}$  in the reaction mixture (Figure 9, curves 3, 4, 5).

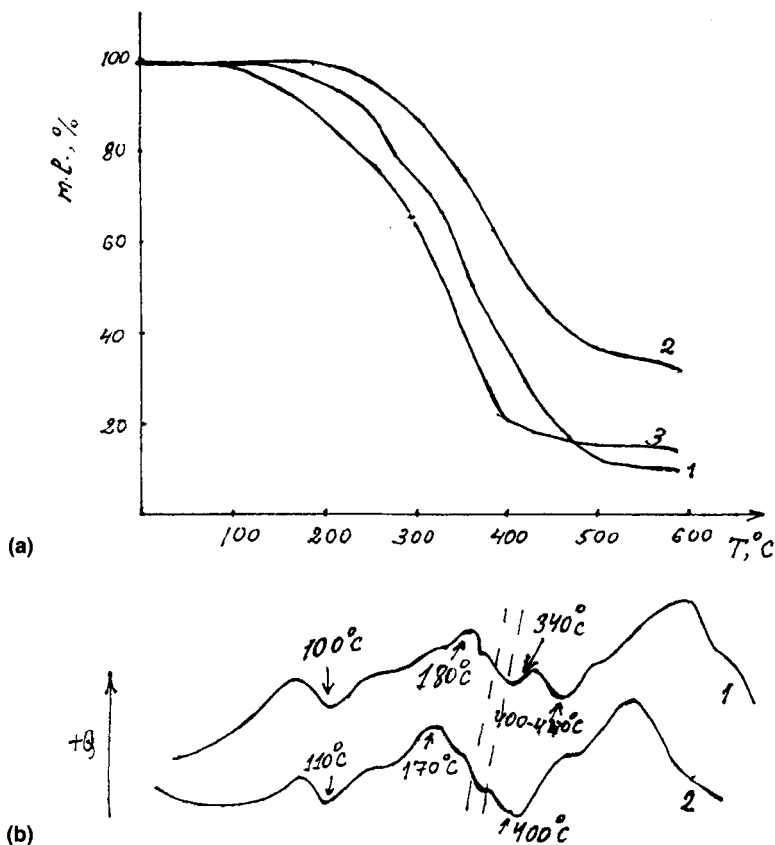


FIGURE 10 (a) The curves of thermogravimetric analysis (TGA) (in air): 1.-4FMA-DVEC (90:10 mass%), 2.-8FMA-DVEC (90:10 mass%), 3.-4FMA-MMA (42,9:57,1 mol.%). (b) The TGA curves for co-polymers of DVEC with: 1.-3FMA (10 mass%), 2.-4FMA (10 mass%).

The research of thermo-oxygenational stability of co-polymers  $n_1$ FMA-MMA demonstrates that the beginning of their thermo-oxygenational destruction is higher than 220°C, developing in the 280–380°C, temperature interval and depending, like case of co-polymers with DVEC, on the molar ratios of  $n_1$ F(M)A (Figure 10a) in the reaction medley.

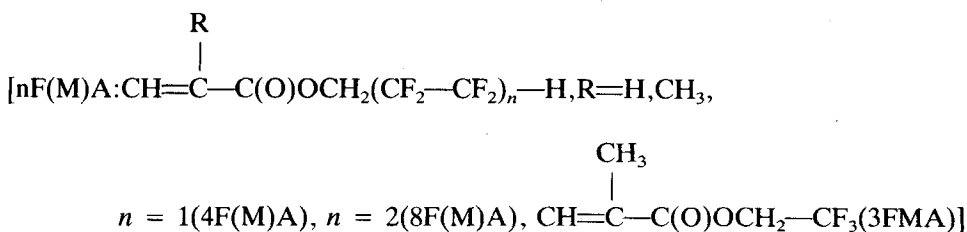
Thermo-oxygenational destruction of co-polymers  $n_1$ FMA-DVEC begins (in air) at  $t > 250^\circ\text{C}$ , it is higher than the beginning of disintegration in air of DVEC homopolymer. The noticeable influence on the thermo-oxygenational stability of PSt by the presence of  $n_1$ F(M)A links in its macromolecular chain is not observed.

The curves of the differential thermic analysis (DTA) of co-polymers  $n_1$ FMA-DVEC are shown in (Figure 10b). There appeared to be some endothermic and exothermic peaks in the different temperature intervals, particularly in the regions 100–110°C, 250–300°C, 400–450°C (endotherm) and 170–200°C (exotherm). The appearance of the first endothermic peaks, apparently coincides with the copolymer's melting, and the second peak at 250–300°C region coincides with the beginning of thermo-oxygenational destruction (10% mass losing). Thermo-ox-

xygenational destruction takes place rapidly in temperature interval 350–450°C almost with the full disintegration of the co-polymer. This rapid disintegration takes place after the process of the air oxygen uptake in temperature interval of (170–200°C).

## CONCLUSIONS

The reaction of co-polymerization of perfluoroalkyl(meth)acrylates



with each other and MMA, styrene(ST) and dimethylvinylethynylcarbinol (DVEC) are studied.

Based on the determination of the constants of co-polymerization  $r_{ij}$  and  $r_{ji}$ , the distribution of the monomers diads, the reaction speeds, the calculation of quantum chemical parameters of double bond of vinyl group, the reactivity of  $n_i\text{F(M)A}$  with the above-mentioned monomers is determined. In the case where couples of monomers  $n_i\text{F(Mi)A-MMA}$ ,  $n_i\text{FMA-St}$ ,  $r_{ij}$  and  $r_{ji}$  are less than one there is a tendency of monomer links to interchange in the macromolecular chain. Determination of probabilities of distributions of the diades shows the statistic process of co-polymerization. In the case of couples where  $n_i\text{FMA-}n_i\text{FA}$  and  $n_i\text{F(M)A-DVEC}$   $r_1 > 1$ ,  $r_2 < 1$ , the preferential addition of increasing radical  $R_{\text{FMA}}$  with its monomer is confirmed. As a result, these co-polymers are enriched with the links of  $n_i\text{F(M)A}$  at small conversions.

Based on the developed computed and experimental data, there are identified suitable couples of monomers ( $n_i\text{FMA:MMA}$ ,  $n = 1,2$ ) to produce the most homogeneous copolymers.

The optical and thermomechanical properties and the thermo-oxygenational stability of the obtained co-polymers were studied. It is established that the thermomechanical properties and thermostability of co-polymers depend on the structure and ratio of fluoroalkyl(meth)acrylates to other vinylcontaining monomers.

## Acknowledgment

We would like to thank Professor V. V. Zaytseva for her help in studying the kinetics of co-polymerization of  $n\text{F(M)A}$  with MMA and discussing the results.

**References**

1. V. M. Levin and A. S. Chegolya, IV international symposium on man-made fibres. PREPRINTS. Kalinin, **6**, 78–90 (1986).
2. L. P. Asatiani, N. G. Lekishvili, G. M. Rubinstein and V. S. Chagulov, The functional classification of optical purposed polymeric materials, Tbilisi, **82** (in Russian) (1990).
3. N. G. Lekishvili, V. V. Zaytseva *et al.*, Bulletin of the Academy of Sciences of the Georgian SSR, **139**, 513–516 (in Russian) (1990).
4. G. S. Goldyn *et al.*, *J. A. Chemistry*, **58**, 1379 (in Russian) (1985).
5. Analysis of Polymerizational Plastmasses. L., 304 (1988)(in Russian).
6. A. M. Toroptseva, K. V. Vologorodskaya and I. M., Bondarenko Laboratories practicum on chemistry of high-molecular compounds, Moscow; Publ. 'Khimia,' (in Russian) (1972).
7. F. Tudos *et al.*, *Kinetics and Catalysis Letters*, **2**, (1975), 439–447.
8. I. E. Eyzner, and B. L. Erusalimsky, Electronic aspect of reactions of polymerization, Publ. 'Nauka,' L., (1976), 65–79 (in Russian).
9. R. I. Makushka, G. I. Bayoras and S. M. Budrene, High-molecular compounds AXXIX N4, 685–691 (1987) (in Russian).
10. R. Alfrey, D. Barer and G. Mark, Co-polymerization, MNP.L 265 (1953) (in Russian).
11. N. G. Lekishvili, L. P. Asatiani, M. G. Kezerashvili, N. B. Grdzeldze and Ts. M. Saraidarova, V polymeric optical materials all-union conference, Leningrad, **37**, (1991) (in Russian).
12. L. Bellami, Infrared spectroscopy of difficult molecules, M.I.L. (1963) (in Russian).
13. V. I. Klenin, S. I. Schegolev and V. I. Lavrushkin, Characteristic functions of light diffusion of dispersional systems. Under Redaction of S.I. Frenkel. Saratov: Saratov University Publ., **12** (1977) (in Russian).