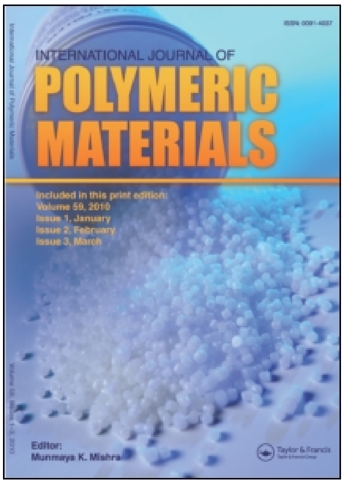


International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Synthesis and Investigation of Properties of the Optically Transparent Carbochain Copolymers with Elementorganical and Hydroxy Groups in the Side Chain of Macromolecules

N. Lekishvili[a]; L. Asatiani[a]; N. Andguladze[a]; G. Lekishvili[a]; T. Guliashvili[a]
[a] Chemical Department, Tbilisi State University, Tbilisi, Georgia

To cite this Article Lekishvili, N. , Asatiani, L. , Andguladze, N. , Lekishvili, G. and Guliashvili, T.(1998) 'Synthesis and Investigation of Properties of the Optically Transparent Carbochain Copolymers with Elementorganical and Hydroxy Groups in the Side Chain of Macromolecules', International Journal of Polymeric Materials, 39: 3, 237 — 253

To link to this Article: DOI: 10.1080/00914039808039771

URL: http://dx.doi.org/10.1080/00914039808039771

Intern. J. Polymeric Mater., 1998, Vol. 39, pp. 237–253
Reprints available directly from the publisher
Photocopying permitted by license only

Synthesis and Investigation of Properties of the Optically Transparent Carbochain Copolymers with Elementorganical and Hydroxy Groups in the Side Chain of Macromolecules

N. LEKISHVILI, L. ASATIANI, N. ANDGULADZE,
G. LEKISHVILI and T. GULIASHVILI

Chemical Department, Tbilisi State University,
3 Chavchavadze av. 380028 Tbilisi, Georgia

(Received 20 October 1996; In final form 10 May 1997)

The carbochain co-polymers with elementorganical and hydroxy groups in the side chain of macromolecules have been synthesized. The reactions of the radical co-polymerization of perfluoroalkyl(meth)acrylates and siliconorganic methacrylates with dimethylvinylacetylenylcarbinol in mass were studied. By using NMR-^{1}H spectroscopy of high resolution, UV, IR spectroscopy and GLC methods the structure and the composition of co-polymers, constants of copolymerization $r_{ij}r_{ji}$, the distribution of homo and heterodiads in macromolecular chain of the co-polymers were determined. The optical, thermomechanical properties and the thermooxidative stability of the co-polymers were researched. The possibility of their application for production of the optical adhesives was determined.

Keywords: Fluoromethacrylates; organosilicon methacrylates; vinylacetylenylcarbinol; reactivity; light conduction; optical adhesives

INTRODUCTION

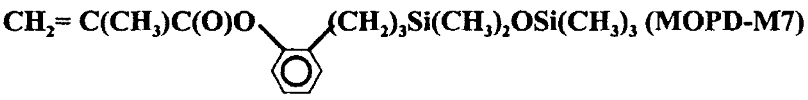
The optical adhesives on the base of dimethylvinylacetylenylcarbinol (DVAC-M_1) have been already described [1,2]. Despite some of their remarkable properties, they have low damping and poor thermostability, and in some cases, poor frost resistance, therefore, their application is limited. One ways to eradicate the above-mentioned shortcomings of these polymers based on DVAC is their modification via co-polymerization of DVAC with the different elementorganic monomers [1].

Therefore, the investigation of the reactions of the radical co-polymerization of fluoro- and siliconorganic (meth)acrylates with DVAC seemed justified. To ascertain the dependence of some of important properties, e.g. the optical and thermomechanical properties and thermooxidative stability on the composition of initial monomers mixtures, along with the co-polymerization conditions that often determine the correct choice of monomers for co-polymers for optical applications [2, 3].

THE INITIAL MONOMERS AND METHODS

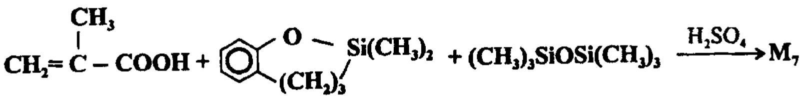
From fluorocontaining monomers we selected the most available perfluoroalkyl(meth)acrylates:1, 1, 3-trihydrotetrafluoropropylmethacrylate $CH_2{=}C(CH_3)C(O)OCH_2(CF_2)_2H(F_4MA{-}M_2)$, and acrylate $CH_2{=}CH{-}C(O)OCH_2(CF_2)_2H(F_4A\text{-}M_3)$, also, 1, 1, 5-trihydrooctafluoroamylmethacrylate$CH_2{=}C(CH_3)C(O)OCH_2(CF_2)_4H(F_8MA{-}M_4)$, obtained by interacting (meth)acryloylclorides with perfluorized alcohols [4].

For siliconorganic methacrylates (SOMA) we used the following monomers: methacryloyloximethylpentamethyldisiloxane $CH_2{=}C(CH_3)C(O)OCH_2Si(CH_3)_2OSi(CH_3)_3(MMPD{-}M_5)$; methacryloyloxibutylpentamethyldisiloxane $CH_2{=}C(CH_3)C(O)O(CH_2)_4Si(CH_3)_2\ OSi(CH_3)_3$ $(MBPD{-}M_6)$; and methacryloyloxyphenyltrimethylenepentamethyldisiloxane



$CH_2{=}C(CH_3)C(O)O{-}C_6H_4{-}(CH_2)_3Si(CH_3)_2OSi(CH_3)_3$ (MOPD-M7)

M_5 and M_6 were obtained by the methods described in the works [5, 6]; M_7 was obtained in accordance with the scheme:



The composition and the structure of the M_7 was established using the data of elementary analysis and IR spectrum (Fig. 1). The monomers were purified directly before co-polymerization using the standard methods [4,6]. They contained not less than 99,6 mass p.c. of the essential substances.

The IR, UV and ^{1}H-NMR spectra were recorded with the spectrometers IR-20, "Specord" and "Perkin-Elmer" ($CDCl_3$, TMS, 298 K) accordingly. The optical properties of the co-polymers in the visible range were researched by using "Specol-11". The thermomechanical properties were studied using the Kargin scale at a heating speed of 1–2 grad./min. The thermooxidative stability (TGA, DTA) was determined using in air at the heating speed of 5 grad./min.

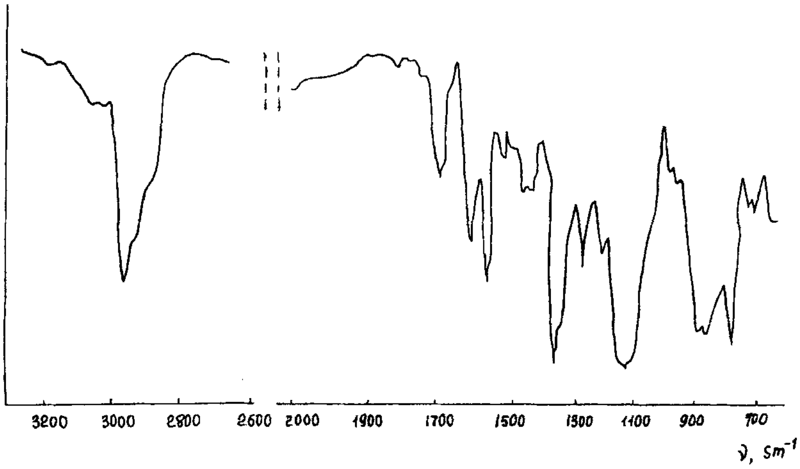


FIGURE 1 IR-spectra of the siliconorganic (meth)acrylate M_7.

RESULTS AND DISCUSSION

1. Radical Co-polymerization of the Silicon and Fluorecontaining(meth)acrylates with Dimethylvinylacetylenylcarbinol and the Structure of the Co-polymers

The reactions of co-polymerisation of perfluoroalkyl(meth)acrylates and siliconorganic methacrylates with DVAC were carried out in mass, in dried argon medium, in presence of azo-bis(isobutyronitryl) (AIBN) and dicyclohexylperoxydicarbonate (DPDC) with quantity of 0,8 mass p.c. The co-polymers were purified by reprecipitation with hexane from the diluted solutions in acetone.

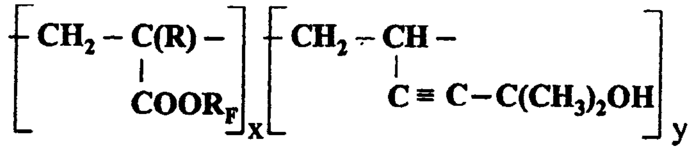
The co-polymers of perfluoroalkyl(meth)acrylates with DVAC(M_1) are optically transparent products, soluble in acetone, chloroform and cyclohexanon. They are not soluble in water, hexane, heptane, methanol and ethanol.

They formed hard transparent films (with $n_D^{20} = 1,440-1,490$) from their solutions after evaporation of the solvent and have good adhesion to poly(vinylalcohol), polystyrene and silica glass surfaces. Molecular masses of the co-polymers were $0,30-0,56 \times 10^5$ ($[\eta] = 0,23-0,38$ dl/g).

The structure and the composition of the co-polymers were determined by using the data of the elemental and spectral analyses. In the IR spectra of the co-polymers of perfluoroalkyl(meth)acrylates the absorption maxima in the region of 1630 – 1640 cm^{-1} (ν_{as} of CF_2 in $(CF_2)H$), 2900 – 2910 cm^{-1} (ν_{as} of CH in CH_3) and weak absorption maxima in the region of 2140–2150 cm^{-1} (ν_{as} of $CH_2{=}CH{-}$) are not found, but we detected the absorption maxima in the regions of 1720 – 1750 cm^{-1} (ν_{as} of C=O), 1070 – 1250 cm^{-1} (ν_{as} of CF_2 in $(CF_2)H$), 2900–2910 cm^{-1} (ν_{as} of CH in CH_3) and weak absorption maxima in the region of 2140–2150 cm^{-1} (ν_{as} of $-C{\equiv}C-$) and 3400 – 3500 cm^{-1} (ν_{as} of OH-groups). In the UV spectra the $\lambda_{max} = 236$ nm was found. It can relate to the ester [C(O)O] groups according to [7,8].

In the ^{1}H-NMR spectra we detected the signals of protons with the following chemical shifts 3,5 – 5,6 δ that belonged to the CHF_2 and CH_2CF_2 groups [9].

In accordance with the above-mentioned data of the spectral and elemental analyses (% $F \geqslant 12,0-13,7$) it can be concluded that the macromolecules of co-polymers of F_iMA – DVAC are enriched by fluorine atoms and contain the perfluoro(meth)acrylatic and acetylenic groups in the side chain:



$$\left[-CH_2-\underset{\substack{|\\ COOR_F}}{C(R)}-\right]_x\left[-CH_2-\underset{\substack{|\\ C\equiv C-C(CH_3)_2OH}}{CH}-\right]_y$$

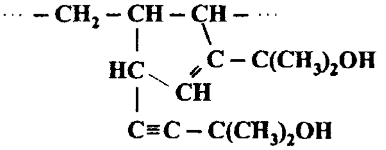
(I)

Where R_F is fluorocontaining radical, $R = H$ or CH_3; x:y depends on the composition of the initial mixture of monomers and on the structure of R_F.

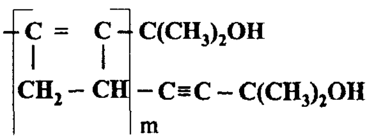
In the case of siliconorganic (meth)acrylates comparatively low molecular co-polymers ($[\eta] \sim 0,18-0,33$ dl/g) are obtained. They form on the above mentioned surfaces (PVA, PS, Silica glass) optically transparent elastic films with $n_D^{20} = 1,470-1,510$. Their adhesion properties and refraction indexes noticeably decrease with the increase of the ratio of methacrylate in the initial monomers' mixture. It should be noted, that, with increasing siliconorganic fragments in alcohol radicals of the monomers, solubility of the co-polymers in usual organic solvents (benzene, acetone, chloroform etc.) decreases. It is linked to the elevation of the energy of intermolecular interaction due to association of disiloxane chains [6].

In the IR spectra of the co-polymers of the siliconorganic methacrylates with DVAC we found the absorption maxima in the regions of 3100 – 3000 cm^{-1} (ν_{as} of CH in C_6H_5), 2890 – 2900 cm^{-1}(ν_{as} of CH in C_6H_5), 3400 – 3600 cm^{-1}(ν_{as} of OH). The weak absorption maxima in the regions of 1060 – 1070 cm^{-1}, 2150 – 2160 cm^{-1}, 1565 cm^{-1}, 1618 cm^{-1} belong to ν_{as} of the disiloxane groups asymmetric substituted acetylenic groups and to ν_{as} of —C=C— groups in the substituted cyclopentens and cyclobutens according to [10, 11]. In UV spectra of all of these co-polymers we detected $\lambda'_{max} = 236$ nm, also $\lambda''_{max} = 226 - 228$ nm characterizing the conjugated double bonds and polyenic compounds [11]. The weak signals with chemical shifts of $4,2 - 5,2\ \delta$ were also found in ^{1}H-NMR spectra which should be associated to the protons of these groups: —CH—C=C—, —CH—C≡C— [12].

Using the literature data [13, 14] of DVAC-homopolymer as a model system for spectral analysis and for ascertaining the structure of the obtained co-polymers, one can assume that the main chain of co-polymers of siliconorganic methacrylates and DVAC contains not only the linear (the I-type structure), but also the cyclic fragments with double bonds. The cyclic fragments can be formed via interaction of the primary radicals of DVAC with the "own" monomers producing the possible structures of the following two types:



II [13]



III [14]

It should be noted, that due to overlapping of their absorption maxima (IR spectra) it is difficult to determine the relation of low intensive $\nu_{as}(-C\equiv C-)$ to the structures of the first (I), second (II) and third (III) types.

The formation of any structure (I or II and III) is likely to depend on the relative reactivity of elementorganic (meth)acrylates in the radical co-polymerization with DVAC as well as on the condition of co-polymerization [11].

The reaction was carried out in the wide range of the composition of initial monomers mixture (10–90 mass p.c.) for evaluation of the relative reactivity of the used elementorganic (meth)acrylates in radical co-polymerization with DVAC and for determination of the distribution of monomer diads in macromolecular chains of the copolymers. Using the (G.L.C.) data of the composition of co-polymers, we obtained the curves of the dependence of m_i molar ratio of monomers links of M_i in co-polymers on the composition of the monomer initial mixture (Fig. 2); r_{ij} and r_{ji} (Tab. I) were determined by the method of Faineman-Ross [5].

As it is evident from Figure 2, for these systems, the macromolecular chain is enriched by the links of the more active component-fluoro(meth)acrylates. The analysis of the distribution of diads (Fig. 3)

TABLE I Some parameters of the co-polymerization DVAC with F_iMA

Perfluoro(meth)acrylates	r_{ij}	r_{ji}	$r_{ij} \cdot r_{ji}$	$1/r_{ij}$	$1/r_{ji}$
F_4MA	$0,55 \pm 0,05$	$1,75 \pm 0,05$	0,92	1,81	0,57
F_8MA	$0,21 \pm 0,01$	$1,43 \pm 0,04$	0,30	4,76	0,69
F_4A	$0,72 \pm 0,12$	$1,20 \pm 0,07$	0,86	1,42	0,80

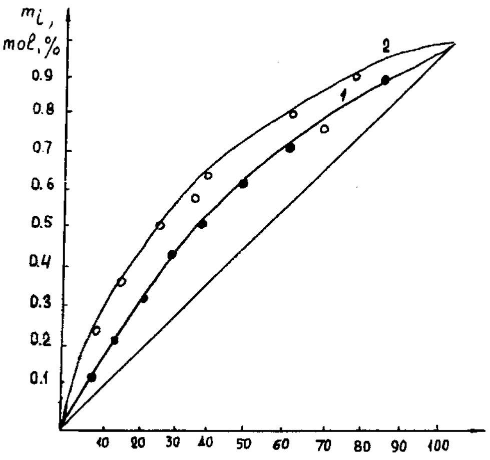


FIGURE 2 The dependence of the co-polymers composition on the composition of the initial monomers mixture in the systems: 1. F_4MA-DVAC, 2. F_8MA-DVAC (M_i-F_iMA).

indicates that the ratio of homodiads $M_j - M_j$ in these co-polymers is higher than that of heterodiads for the pair of monomers F_iMA-DVAC.

As it was expected, DVAC (in comparison with F_4MA and F_8MA) has relatively less reactivity and its radical demonstrates higher activity of interaction with another monomer. So, the probability of formation of the cyclic fragments (II and III) by the interaction of a radical of DVAC with its monomer, is low especially in the initial stage where the formation of the macromolecular chain takes place in accordance with I, which is proved by the results of spectral investigations.

The different situation exists in case of the co-polymerization of siliconorganic methacrylates with DVAC. For example, using AIBN as an initiator at the temperature of 80°C, the function of $m_i = f(M_i)$ is

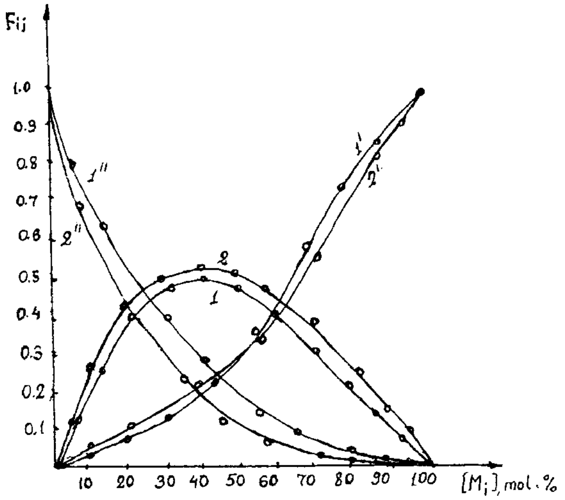


FIGURE 3 The dependence of the hetero-M_i-M_j(1, 2) and homodiads M_i-M_i(1′, 2′) and M_j-M_j(1″, 2″) ratio on the composition of the initial monomers mixture in the systems: 1. F_4MA-DVAC, 2. F_8MA-DVAC 3. F_4A-DVAC.

also different from linear dependence (Fig. 4), but $r_{ij} > 1$ and $r_{ji} < 1$ (Tab. I). This means that the reactivity of increasing radicals M_1^*, relative to the monomer of DVAC is higher than that relative to the siliconorganic methacrylates. As a result, the macromolecular chain of the co-polymers is enriched by the DVAC links.

The content of homodiads $M_i - M_i$ has a higher probability than that of heterodiads (it is demonstrated also by the calculated Harwood parameter *R*, Tab. II). Their total ratio is less than 0.5 in the interval of 35–50 mol. p.c. of M_1 in the initial mixture of monomers (Fig. 5).

The obtained data of the relative activity of $F_i(M)A$ correlate well with those of the quantum chemical calculations (MINDO-3) (Tab. III, Fig. 6). [16, 17].

The study of co-polymerization of the systems M_1-M_2, M_1-M_6 and M_1-M_7 at the equimolar ratio of the monomers demonstrates that the reactions proceed until a practically complete consumption of DVAC. But, for achieving high conversions (> 90%), the relatively prolonged heating of the reaction mixture is indispensable (up to 15–16 hrs at

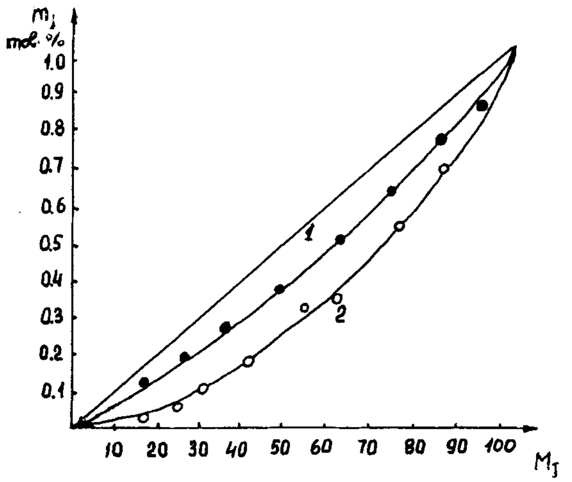


FIGURE 4 The dependence of the co-polymers composition on the composition of the initial monomers mixture in the systems: 1.-DVAC-MMPD 2.-DVAC-MBPD.

TABLE II Some parameters of co-polymerization of DVAC (M_1) with M_5, M_6 and M_7 (the initiator AIBN-0,8 mass. p.c., reaction temperature = 80°C)

co-monomers	r_i	r_j	$r_j \cdot r_i$	$1/r_i$	*Parameter of Harwood, R*
M_5	$3,35 \pm 0,03$	$0,52 \pm 0,05$	1,74	0,30	40,0
M_6	$4,02 \pm 0,06$	$0,28 \pm 0,05$	1,13	0,25	43,8
M_5^*	$2,64 \pm 0,02$	$0,63 \pm 0,04$	1,68	0,37	35,0
M_7	$2,31 \pm 0,05$	$0,48 \pm 0,03$	1,11	0,43	45,6

*DPDC-initiator 0, 8, mass. p.c.

80°C). In all these cases, the reactions have a small induction period (Fig. 7), their durations are determined by the structure of alcohol radical of elementorganic (meth)acrylate. It should be noted, that the influence of steric hindrance at α-carbon of the double bond of vinyl group is higher in M_7, than in M_6. Nevertheless, the maximal velocity of reaction in the above mentioned ratios of the monomers is higher for the system, M_1-M_7, than for M_1-M_6. It can be explained with the increase of polarity of vinyl groups of M_7 monomer and of energies of chain cutting in the first case. The maximal velocity (on the stage of the autoacceleration) of co-polymerization calculated on

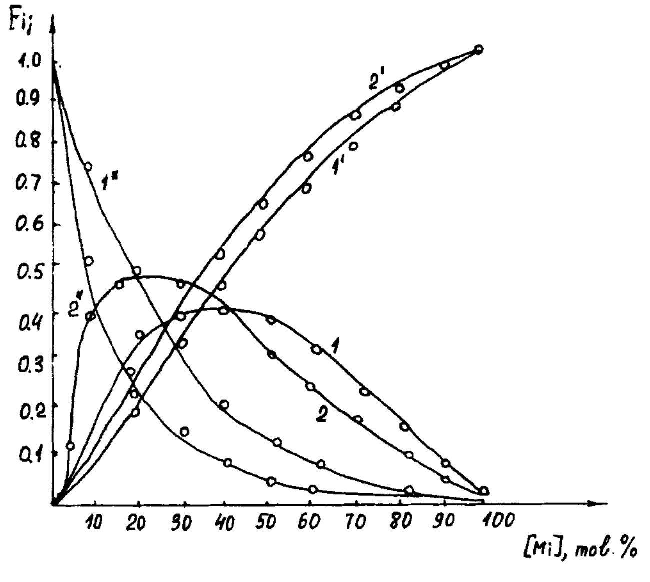


FIGURE 5 The dependence of the hetero-M_i-M_j(1, 2) and homodiads M_i-M_i(1′, 2′) and $M_j - M_j$(1″, 2″) ratio on the composition of the initial monomers mixture in the systems: 1.-DVAC-MMPD (1, 1′, 1″) 2.-DVAC-MBPD (2, 2′, 2″).

TABLE III The data of the quantum-chemical calculation of DVAC and F_iMA

Monomer	q^{β}	$P^{\pi+\delta}_{c=c}$	$P^{\pi}_{c=c}$	$W_{c=c}$	$F_{c\beta}$	E_{full}, eV
DVAC	− 0,057	1,920	0,989	0,915	0,741	− 1345,33
F_4A	+ 0,071	1,895	0,970	1,890	0,762	−3389,68
F_4MA	+ 0,050	1,871	0,950	1,866	0,782	− 3540,24

the basis of the kinetical curves (Fig. 7) is 3,2 p.c. min^{-1} for the system M_1-M_2.

2. The Optical, Thermomechanical Properties, Thermooxidative Stability and Use of Co-Polymers

The optical properties of the obtained co-polymers were studied using the spectrophotometer "SPECOL-11" during the process of co-polymerization

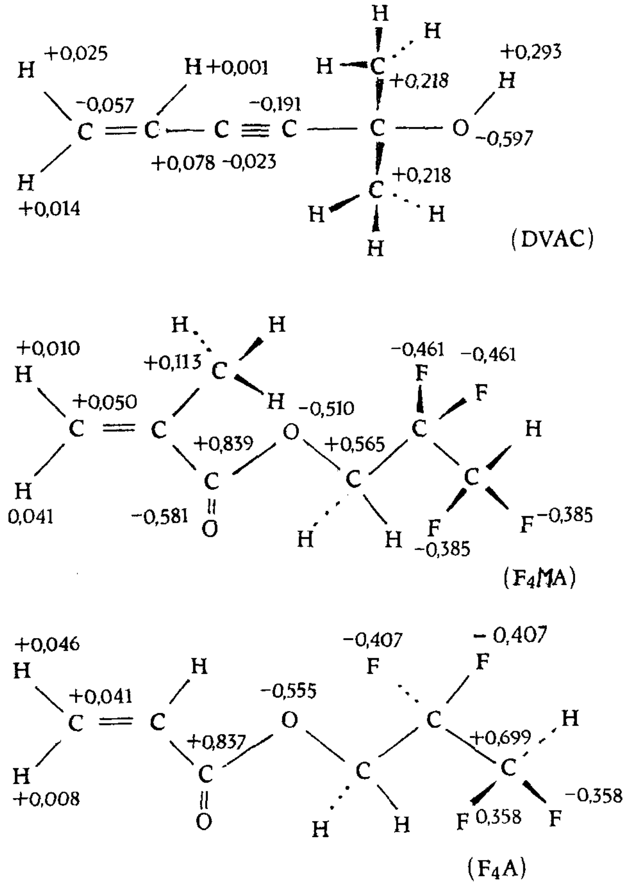


FIGURE 6 The spatial structure and the charges on the atoms of the molecules DVAC, F_4MA, F_4A.

for the compositions of the initial mixture of the monomers containing methacrylates ⩽ 30 mol %. The investigations were performed in the glass containers with the size of 25,0 × 25,0 × 1,0 m.m., at the temperatures 80 and 100°C using the special camera which had "windows" for light passing. The obtained data were worked up with the method of "spectral turbidity" [17, 18]. The magnitude of coefficient of turbidity τ_t depends on the structure of methacrylates, on the composition of the initial mixture of monomers, on the wavelength (Tab. IV) and on

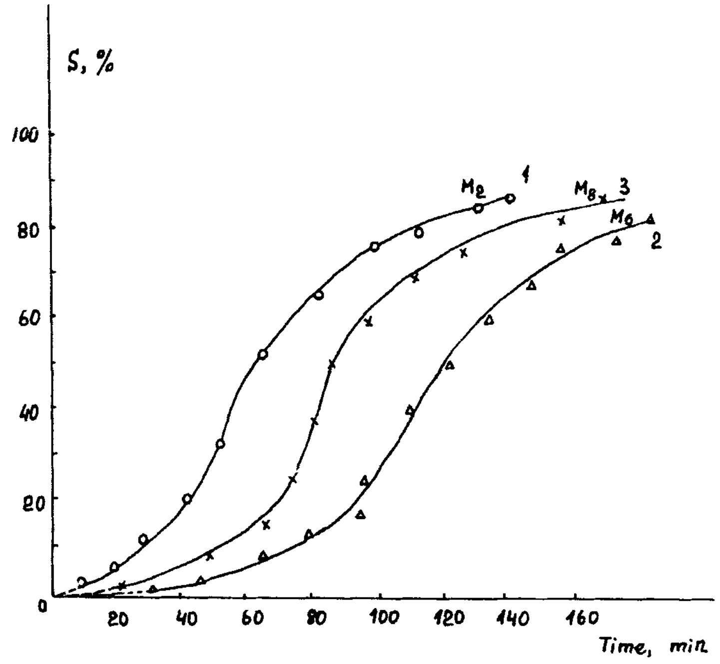


FIGURE 7 The kinetical curves of the systems: 1. -F_4MA-DVAC, 2. -MOPD-DVAC and 3.-MBPD-DVAC ($T_{reac.} = 80°C$). (The conversion of the monomers was determined gravimetrically. S% is the yield of the co-polymers).

the condition of co-polymerization [11, 17]. By decreasing the ratio of fluoro(meth)acrylates in monomers mixture, τ_t is decreased. The same phenomenon is observed at the decrease of the length of the fluorocontaining fragment in the alcohol group of methacrylate. Carrying out the reaction at the temperature higher than 100° and continuing the reaction up to the high level of conversion (>95 p.c.) an increase of τ_t (e.g. from 0,112 till 0,311 at $\lambda = 500$ n.m., F_4MA-DVAC) is observed. It can be explained with the poor optical compatibility of the co-polymer with the forming homopolymer of DVAC of high n_D due to the disappearance of the more active perfluoroalkylmethacrylate at the deepest stage of polymerization. The yellowing of the patterns also takes place using the peroxide initiators, particularly benzoyl peroxide, instead AIBN. The light-conductivity of F_i(M)A-DVAC decreases to (53–58 %) with the dimness of the investigating

TABLE IV The optical properties of co-polymers FMA MBPD with DVAC (t_{reac} = 80°C; init.-AIBN 0,8 mass. p.c.)

Composition of co-monomers, mol.%	*koef. of turbidity, τ_t, cm^{-1}* 350 *m.m.*	500 *m.m.*
DVAC-4FMA (90:10)	1,316	0,032
DVAC-8FMA (90:10)	1,312	0,057
DVAC-4FMA (80:20)	1,329	0,094
DVAC-8FMA (80:20)	1,335	0,112
DVAC-MBPD* (80:20)	1,749	1,012

patterns by heating them for a long time in air at $t > 100°C$. The values of the turbidity constants of the co-polymers decrease (the light conducting is increased) with the increasing wavelength λ from 350 to 500 n.m. (Tab. IV). In comparison with the co-polymers of perfluoroalkyl(meth)acrylates and DVAC, the co-polymers of the siliconorganic methacrylates have higher turbidity values (Tab. IV). That can be explained with the poor compatibility of the corresponding monomers and also with the co-polymers and the homopolymer of poly(meth)acrylate formed in the later stages of the co-polymerization. The yellowing of these co-polymers, which are obtained at high conversions (> 95%), is explained by the above mentioned cyclic structures.

The thermomechanical curves of the obtained co-polymers (Fig. 8) are characteristic (typical) for the thermoplastic polymers. The temperature of vitrification depends on the structure of methacrylates and the ratio of the molar concentration of the monomers in the initial mixture. By increasing the chain length of the fluorocontaining fragment and quantity of fluoroatoms, T_{vit} of the co-polymers decreases. The opposite effect takes place in the case of co-polymers of α-fluoroperfluoroalkylacrylates with DVAC (Tab. V). The largest shift of T_{vit} towards low temperatures in comparison with homopolymer is observed with the co-polymers of siliconorganic methacrylates and DVAC. By increasing the ratio and the length of siliconorganic fragments in co-polymers, T_{vit} decreases.

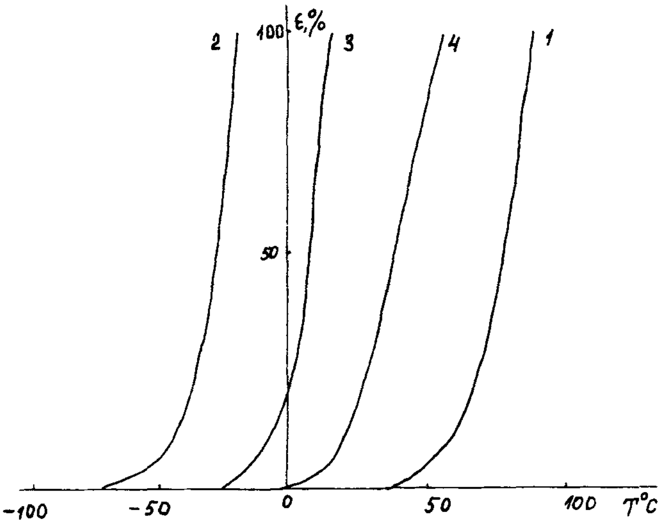


FIGURE 8 Thermomechanical curves of co-polymers: 1. Homopolymer DVAC 2. DVAC-MBPD (10:90 mol%) 3. DVAC-MBPD (30:70 mol.%) 4. DVAC-F_8MA (20:80 mol. %).

TABLE V Some properties of optical adhesive composite in the optical element based on CH_2-C(F)C(O)OCHF—CF_2H and DVAC(15:85 mass. p.c.)

The working temperature interval °C	*Dampresitence (in special camera,* at $t = 40$°C *and* 98 *p.c. of humidity)*	*Viscosity, P a.s.*	*Thermostability* (10 *p.c. mass, Less*), °*C*
– 60 ÷ 95°	21	0, 2 – 0.3	230

The investigation of the thermooxidative stability of the co-polymers indicated the dependence of this property on the nature of alcohol radical of the methacrylates (Fig. 9). By increasing the length of the fluorocontaining fragment and the quantity of the fluoroatoms of the alcoholic radical of methacrylate, the temperature of the beginning of the thermooxidative destruction (comparing with the according temperature of the homopolymer) increases and the essential process of the thermooxidative destruction is shifted towards a higher temperature range (Fig. 9. 360–400°C) [19]. In the case of the co-polymers of the siliconorganic methacrylates and DVAC, the temperature of the destruction onset is lower than that of the co-polymers of fluoroalkylmethacrylates. In the present case, however the increasing

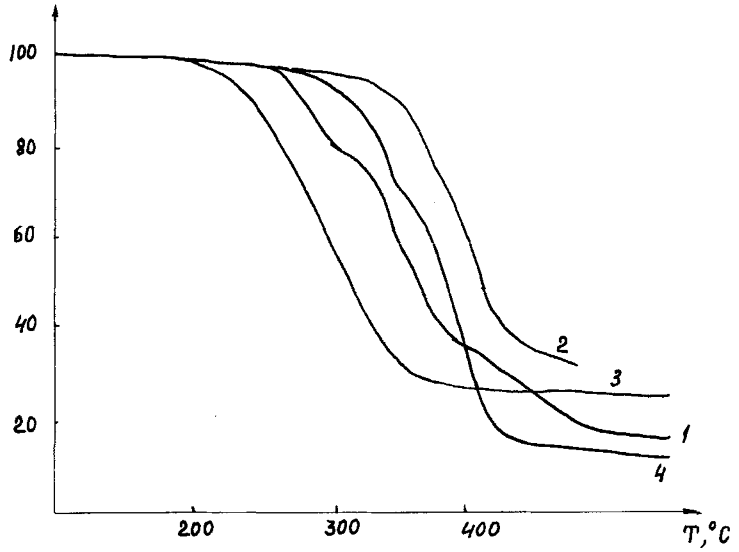


FIGURE 9 The curves of thermogravimetric analysis (TGA, on air) of co-polymers: 1. F_4MA-DVAC (90:10 mass. %) 2. F_8MA-DVAC (90:10 masss. %) 3. DVAC-MBPD (90:10 mass.%) 4. DVAC-F_8MA (30:70 mass %).

of the length of the siliconorganic fragment in the main chain of the co-polymer with $(—CH_2—)_4$ group produces no significant effect on the thermooxidative destruction . In spite of the content of the cyclolinear fragments based on DVAC, the intense thermooxidative destruction takes place in the temperature interval of 320–350°C with the practically complete destruction of the co-polymers sample.

Several elaborated optical adhesives based on the obtained co-polymers [1, 20] were developed.

These compositions are used to join the optical polarization elements of poly(vinyl-alcohol), as well as, other parts of optical communication.

It is also noteworthy, that some of the synthesized polymers can be applied as light reflecting layers of optical polymers and glass fibers.

CONCLUSION

The radical co-polymerization of the fluoro-and siliconorganic (meth) acrylates with dimethylvinylacetylenylcarbinol (DVAC) has been carried out. Based on the obtained experimental data, the constants of co-polymerization r_{ij}, r_{ij}, the distribution of the monomeric link diads in the macromolecular chain of the co-polymers and the parameter of Harwood (R) were determined. Using the data of IR, UV and 'H-NMR spectra we established, that in the case of perfluoro(meth)acrylates the macrochains of the co-polymers are enriched with the links of the more reactive fluorocontaining monomers. In the case of siliconorganic methacrylates the main chain of the co-polymers contains the cyclic links of carbinol, which can be formed via interacting the primary radicals of DVAC with its "own" monomers. The dependence of the optical, thermomechanical properties and thermoxidative stability on the structure of the alcohol radicals of the methacrylates, on composition of the inital mixture of the monomers and on conditions of co-polymerization was established.

Acknowledgement

Prof. N. Lekishvili, Dr. T. Guliashvili and G. Lekishvili express their gratitude to the International Soros Education Foundation for its Grants.

References

[1] Lekishvili, N., Asatiani, L., Saraidarova, Ts. and Kezherashvili, M. G. (1991). Ser. USSR No. 4856684/04.

[2] Lekishvili, N., Rubinstein, G. and Asatiani, L. P. (1994). Polymeric Conductors of Light: Receive, Possibility, Use., Publ. TSU, Tbilisi, 134. (in Russian).

[3] Asatiani, L., Lekishvili, N., Rubinstein, G. and Chagulov, V. The functional classification of optical purposed polymeric materials. Tbilisi, Publ. TSU. 82. (in Russian).

[4] Goldin, G. S. *et al.*, I. A. Chemistry, **58**, 1379 (in Russian).

[5] Merker, R. L. and Noll, J. E. (1956). *J. Org. Chemistry*, **21**(12), 1337.

[6] Adrianov, K. A., Volkova, L. M., Zhdanov, A. A. and Parsegova, E. P. (1980). *J. G. Chem.* TL (C XII), 1088 (in Russian).

[7] Analysis of Polymerizational Plastmasis, L. 304 (1988). (in Russian).

[8] Bellami, A. (1963). Infrared Spectroscopy of difficult molecules. M.II. (in Russian).

[9] Lekishvili, N., Zaitseva, V. V. *et al.* (1990). *Bull. of the Acad. Sci of Georgia*, **139**(3) 513–516 (in Russian).

[10] Silverstein, R., Basler, B. and Norril, T. (1977). The Spectroscopy Identification of Organic Compounds. M. F. L. p. 157 (in Russian).

[11] Lekishvili, N., Andguladze, N., Tsomaia, N. and Asatiani, L. (1995). *Bull. of the Acad. Sci. of Georgia*, **152**(3), 537–541 (in Georgian).

[12] Ioramashvili, D. (1983). The Kinetical NMR-Portraits of Chemical Reactions. "Metsniereba", Tbilisi p. 374.

[13] Chaltikian, O. A. (1968). Success of Chem. Polymers in the Armen. SSR, In book: Kinetics and Mechanism Formation and Transformation of Macromolecules. M. "Nauka", 289 (in Russian).

[14] Nazarov, N. N. (1961). Selected works. M. Publ. A. S. of USSR, p. 147.

[15] Alfrey, R., Borer, D. and Mark, G. (1953). Co-polymerization. MNP, L. p. 265 (in Russian).

[16] Lekishvili, N., Asatiani, L., Guliashvili, T., Kejerashvili, M. and Khuroshvili, D. (1993). *Bull. of the Acad. of. Sci. of Georgia*, **143**(2), pp. 234–237 (in Russian).

[17] Lekishvili, N., Asatiani, L. *et. al.* (1995). *Intern Journ. of Polym. Mater*, **27**, pp. 163–174.

[18] Kleinin, V. I., Schegolev, S. I. and Lavrushkin, V. I. (1997). Characteristic functions of light diffusion of dispersional Systems. Under redaction of S. I. Frenkel. Saratov, Univers. Publ. p. 12 (in Russian).

[19] Lekishvili, N., Guliashvili, T., Asatiani, L. *et al.* (1993). *Proceeding of the Acad. of Sci. of Georgia*, **19**(1–2), 193–201 (in Georgian).

[20] Lekishvili, N., Kezherashvili, M., Grdzelidze, N. *et al.* (1991). The All-Union seminar on optical polymeric materials Leningrad. Abstracts, p. 37 (in Russian).