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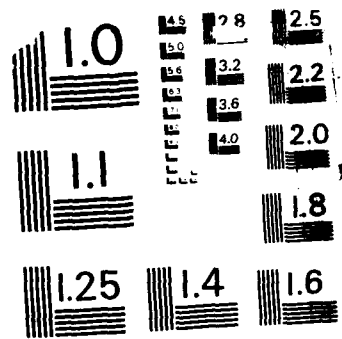
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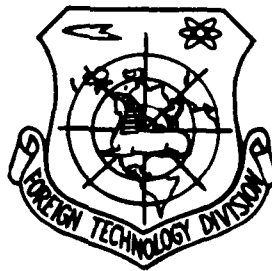
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## HUMAN TRANSLATION

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Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	У у	<i>У у</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

\*ye initially, after vowels, and after Е, е; elsewhere.  
When written as ѐ in Russian, transliterate as yě or ě.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	$\sinh^{-1}$
cos	cos	ch	cosh	arc ch	$\cosh^{-1}$
tg	tan	th	tanh	arc th	$\tanh^{-1}$
ctg	cot	cth	coth	arc cth	$\coth^{-1}$
sec	sec	sch	sech	arc sch	$\operatorname{sech}^{-1}$
cosec	csc	csch	csch	arc csch	$\operatorname{csch}^{-1}$

Russian      English

rot      curl  
lg      log

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## FREE RADICALS GENERATED WITH THE POLYMERIZATION OF METHYL METHACRYLATE IN THE PRESENCE OF NITROALKANES

*A. I. Shreybert, A. P. Kharbin, O. I. Knyazeva and P. G. Tishkov*

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The polymerization of methyl methacrylate (MMA) in the presence of nitroalkanes is accompanied by a decrease in spin-lattice relaxation time even in the absence of a monomer-to-polymer transformation, which is evidently linked to the participation of free radicals in this process [1].

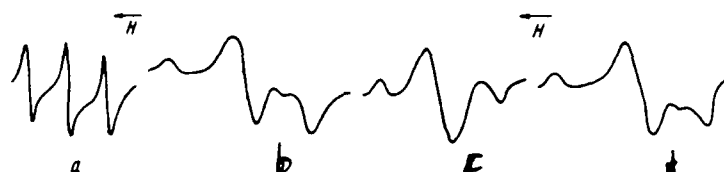
With the objective of elucidating the nature of these free radicals and developing some estimate of their concentration, we undertook to investigate the polymerization of MMA in the presence of tetranitromethane, 1,1-dinitroethane and nitroethane using the electron paramagnetic resonance (EPR) method.

### Experimental procedure

MMA (0.029 mole) was polymerized at 50° in the presence of nitroalkanes: tetranitromethane, 1,1-dinitroethane and nitroethane (0.008 mole). For a number of experiments we also added benzoyl peroxide (0.0006 mole). EPR spectra were recorded using the standard RE-1301 radiospectroscope. We established the concentration of free radicals with respect to diphenylpicrylhydrazyl using the technique of comparing the integral curves of the test sample with those for the standard [2].

## Discussion of findings

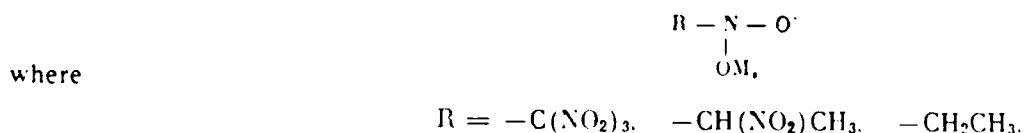
When MMA is polymerized in the presence of nitroalkanes, the EPR signal can be observed within 90-150 min. The EPR spectrum of the free radicals generated with the polymerization of MMA in the presence of tetranitromethane, 1,1-dinitroethane and nitroethane presents us with a triplet. In the case of the tetranitromethane the components of the hyperfine structure (STS [hfs]) are symmetrical, splitting  $\pm 17$  Oe, width 3.4 Oe. The symmetry of the triplet is destroyed by the addition to the MMA-tetranitromethane mixture of benzoyl peroxide, as well as by the polymerization of MMA in the presence of 1,1-dinitroethane, nitroethane and benzoyl peroxide (see figure).



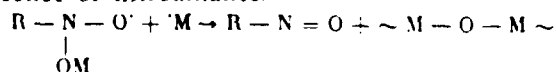
**Figure 1.** EPR spectra of free radicals in the following systems: (a) - MMA + tetranitromethane; (b) - MMA + tetranitromethane + benzoyl peroxide; (c) - MMA + nitroethane + benzoyl peroxide; (d) - MMA + 1,1-dinitroethane + benzoyl peroxide

Analysis of the hfs of the spectrum permits us to hypothesize hyperfine isotropic interaction on the part of the unpaired  $2 p_z$  oxygen electron distributed along the nonhybrid  $2 p$  nitrogen orbit  $N^{14}$ . Since the spin of the  $N^{14}$  nucleus  $I = 1$ , this interaction causes each Zeeman level to split into three sublevels with energies [2]  $\epsilon_0 + A_1 m_1$ , where  $A_1$  is the hyperfine splitting constant and  $m_1 = 1, 0, -1$ .

The EPR spectrum should therefore appear as a triplet comprising equidistant components and correspond to the following radical:



This free-radical structure offers a good explanation of the mechanism involved in retarding the polymerization of MMA in the presence of nitroalkanes:



**Concentration and hfs of free radicals formed with the polymerization of MMA in the presence of nitroalkanes at 50°**

Состав смеси (a)	Время полимеризации, мин. (b)	Количество парамагнитных центров в 1 см <sup>3</sup> (c)	СГС свободных радикалов * (e)			
			Соотношение интенсивностей (d)	$\Delta H$ , э	$\delta H_1$ , э	$\delta H_2$ , э
ММА + тетранитрометан (f)	90	$5 \cdot 10^{14}$	1:1:1:1	3,4	17	17
	150	$9,5 \cdot 10^{14}$	1:1,2:1,1	3,4	17	17
	320	$1,2 \cdot 10^{15}$	1:1,1:1,1	3,4	17	17
ММА + тетранитрометан + + перекись бензоила (g)	100	$6 \cdot 10^{14}$	1:1,2:1,1	3,4	17	17
	130	$9,5 \cdot 10^{14}$	1:1,7:1,7	3,4	17	17
	180	$1,8 \cdot 10^{15}$	1:2:1,9	3,4	17	17
	270	$8 \cdot 10^{15}$	Асимметричный спектр (h)	12	35	35
	360	$1,2 \cdot 10^{16}$	То же (k)	13	35	26
ММА + 1,1-динитроэтан + + перекись бензоила (i)	90	$4,3 \cdot 10^{15}$	» »	13	35	26
	150	$7 \cdot 10^{15}$	» »	13	36	26
ММА + нитроэтан + перекись бензоила (j)	150	$(1-3) \cdot 10^{13}$	» »	11,2	26	26
	300	$2,5 \cdot 10^{15}$	» »	11,2	26	26

**KEY:** (a) - composition of mixture; (b) - polymerization time, min; (c) - number of paramagnetic centers per 1 cm<sup>3</sup>; (d) - ratio of intensities; (e) - hfs of the free radicals\*; (f) - MMA + tetranitromethane; (g) - MMA + tetranitromethane + benzoyl peroxide; (h) - asymmetrical spectrum; (i) - MMA + 1,1-dinitroethane + benzoyl peroxide; (j) - MMA + nitroethane + benzoyl peroxide; (k) - same; \* -  $\Delta H$  - width of component;  $\delta H_1$  and  $\delta H_2$  are splitting values.

The polymer radicals react with the oxygen of the nitro group, which breaks the chain. The mechanism suggested here will evidently be similar to that which we observe in the case of polymerization in the presence of aromatic nitro compounds [3-5].

It is possible that the asymmetry of the triplet and the broadening of the outer components (see figure) are due to anisotropic hyperfine dipole-dipole interaction between the magnetic moments of the N<sup>14</sup> nucleus and an electron, and in the case of the nitroethane and the 1,1-dinitroethane to the high viscosity of the medium.

The polymerization of MMA is accompanied by an increase in the concentration of free radicals. As would be anticipated, the highest concentration will be observed when MMA is polymerized in the presence of tetranitromethane (see table). In a number of experiments it

rose to  $1.2 \cdot 10^{16}$  paramagnetic centers/cm<sup>3</sup>. The intense retarding effect of the tetranitromethane referred to in [1] must be attributed to the high concentration of the inactive free radicals forming the chain. Other conditions remaining equal, the decrease in the number of nitro groups in turn reduces the concentration of free radicals (in the case of the nitroethane it drops to  $(1-3) \cdot 10^{13}$  paramagnetic centers/cm<sup>3</sup>) and, accordingly, the retarding effect as well. It has been possible, for example, to polymerize MMA in the presence of nitroethane and benzoyl peroxide [1]. Therefore, aliphatic nitro compounds, being sources of inactive free radicals, will retard the polymerization of vinyl monomers.

### Conclusions

1. The EPR technique has been used to investigate the polymerization of methyl methacrylate in the presence of tetranitromethane, 1,1-dinitroethane and nitroethane.

2. The polymerization of methyl methacrylate in the presence of nitroalkanes is accompanied by the formation of free radicals; the concentration and hfs of these free radicals has been established.

3. The retarding effect of nitroalkanes on the polymerization of methyl methacrylate has been explained.

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## COPOLYMERIZING COMPLEX ESTERS OF METHYLOYLMETACRYLAMIDE

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USSR Academy of Sciences

Previous investigations have focused on a number of properties of polymers of complex methyloylmetacrylamide esters in both linear and three-dimensional form [1].

The present paper presents findings from a study of the copolymerization of complex methyloylmetacrylamide esters, specifically, the acetic (UEMOL), benzoic (BEMOL) and butyric (MEMOL) esters, with methyl methacrylate (MMA) and acrylonitrile (AN). With the objective of characterizing the reactivity of these esters we established the copolymerization constants  $r_1$  and  $r_2$  for the monomer pairs MMA-MEMOL and AN-MEMOL and computed  $Q$  and  $e$  for MEMOL.

We also established a number of properties of the MMA-UEMOL and MMA-BEMOL copolymers in the final phase of polymerization upon completion of the condensation processes, which were conducted by heating the linear polymers at 130°.

### Experimental procedure

UEMOL and MEMOL were produced by reacting the corresponding acid anhydrides with methyloylmetacrylamide in toluene [2].

For polymerization we selected fractions with a boiling point  $88-89^\circ/2.5 \cdot 10^{-2}$  mm in the case of the UEMOL and  $91-92^\circ/4 \cdot 10^{-2}$  mm in the case of the MEMOL.

To produce the BEMOL we reacted benzoyl chloride with methyloylmetacrylamide; after recrystallization from the petroleum ether it had a melting point of 87°. [3].

We distilled the MMA and selected a fraction with a boiling point of 45°/90 mm. Prior to the reaction the AN was also distilled and a fraction selected with a boiling point of 77°.

**Table 1.** Copolymerization of complex methyloylmetacrylamide esters ( $M_2$ ) with AN ( $M_1$ ) in dimethylformamide solution with 0.2% cyclohexyl ester of percarbonic acid

$M_2$	Исходное соотношение мономеров мол. % (1)		Соотношение смеси мономеров : ДМФА (2)	Степень превращения, % (3)	[ $\eta$ ]	(4) Состав сополимера, мол. % m <sub>1</sub> :m <sub>2</sub>
	$M_1$	$M_2$				
МЭМОЛ (5)	80	20	1:4	32,4	1,44	75:25
То же	90	10	1:2	15,0	—	87:13
» »	95	5	1:5	38	1,62	91:9
» »	97,5	2,5	1:5	46	1,67	90,5:9,5
БЭМОЛ (6)	90	10	1:5	16	1,62	80:20
То же	95	5	1:5	15	1,77	90:10
» »	97,5	2,5	1:5	36	2,1	99:1

KEY: 1 - initial monomer ratio (mol. %); 2 - ratio monomer mixture : dimethylformamide; 3 - degree of conversion; 4 - composition of copolymer, mol. %; 5 - MEMOL; 6 - BEMOL

**Table 2.** Copolymerization of MMA ( $M_1$ ) with MEMOL ( $M_2$ ) (polymerization temperature 70°, initiator - 0.2% benzoyl peroxide)

Опыт. № (1)	Состав исходной смеси, мол. доли (2)		Степень превращения, % (3)	N, %	Состав сополимера, мол. доли (4)	
	$M_1$	$M_2$			m <sub>1</sub>	m <sub>2</sub>
1	0,7875	0,2125	4,19	1,765	0,8588	0,1412
2	0,8091	0,1909	4,2	1,625	0,8712	0,1288
3	0,5353	0,4646	4,8	3,525	0,6796	0,3204
4	0,4777	0,5223	2,56	3,96	0,6377	0,3623
5	0,1905	0,8095	5,06	6,205	0,2893	0,7107
6	0,3492	0,6508	5,8	4,98	0,4898	0,5102

KEY: 1 - experiment; 2 - composition of starting mixture, mole fraction; 3 - degree of conversion; 4 - composition of copolymer, mole fraction

The complex methyloylmetacrylamide esters were copolymerized with the MMA and AN in the presence of peroxide initiators (benzoyl peroxide and cyclohexyl percarbonate) both in bulk and in solution. The copolymers thus produced were purified by reprecipitating the AN-MEMOL and AN-BEMOL products from dimethylformamide solution with methyl alcohol, the MMA-MEMOL, MMA-BEMOL and MMA-UEMOL from acetone with ethyl ether. The composition of the copolymer was established on the basis of the nitrogen content.

**Table 3. Copolymerization of AN ( $M_1$ ) with MEMOL ( $M_2$ ) (polymerization temperature 70°, initiator - 0.2% benzoyl peroxide)**

Опыт. № (1)	Состав исходной смеси, мол. доли (2)		Степень пре- вращения, % (4)	N, %	Состав сополимера, мол. доли (3)	
	$M_1$	$M_2$			$m_1$	$m_2$
1	0,7991	0,2009	5,8	14,95	0,6919	0,3081
2	0,8031	0,1999	6,3	14,54	0,6718	0,3282
3	0,5188	0,4812	5,5	12,08	0,5235	0,4764
4	0,4870	0,5130	5,6	11,1	0,4458	0,5542
5	0,2936	0,7964	5,6	9,29	0,2593	0,7404
6	0,1929	0,8071	5,2	9,15	0,2411	0,7589

**KEY:** 1 - experiment number; 2 - composition of starting mixture, mole fraction; 3 - composition of copolymer, mole fraction; 4 - degree of conversion, %

Tables 1-3 summarize the findings from experiments involving copolymerization in both solution and in bulk. We used the data in Tables 2-3 to compute the copolymerization constant in accordance with the conversion method of Mayo and Lewis [4].

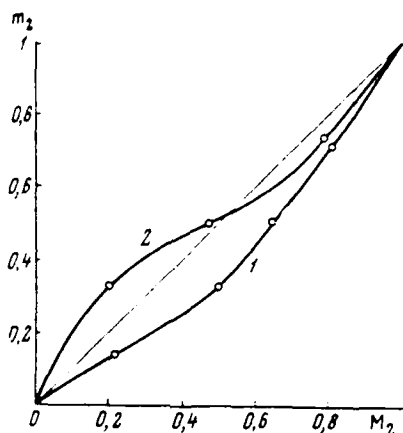
**Table 4. Copolymerization of MMA ( $M_1$ ) with complex methyloylmetacrylamide esters ( $M_2$ ) in the presence of 0.2% benzoyl peroxide**

Эфир метилолметакриламида (1)	УЭМОЛ	ВЭМОЛ
Мольное соотношение мономеров $M_1 : M_2$ (2)	85:15	85:15
Теплостойкость по Вика, °C (3)	135	135

**KEY:** 1 - methyloylmetacrylamide ester; 2 - mole ratio of monomers  $M_1$  and  $M_2$ ; 3 - Vicat heat resistance, °C. Note: Polymerization was conducted at temperature constantly elevated from 45 to 120°.

Table 4 presents findings from experiments involving the copolymerization of MMA with UEMOL and BEMOL in the presence of peroxide initiators at temperatures favorable to the condensation processes.

Results of computations of copolymerization constants are summarized in Table 5 and then graphed in the figure.



**Copolymer composition as function of composition of starting mixture of monomers: 1 - copolymer MMA-MEMOL; 2 - copolymer AN-MEMOL;  $M_2$  - mole fraction of MEMOL in starting mixture of monomers;  $m_2$  - mole fraction MEMOL in copolymer**

#### Discussion of findings

We can see from Table 5 that with any ratio of  $M_1$  to  $M_2$  in the mixture of monomers, the MMA-MEMOL (curve 1) copolymer is always going to be impoverished of MEMOL units ( $r_2 < 1$ ,  $r_1 > 1$ ) and enriched with MMA units. In this instance, the end radical of the polymer chain  $M_1$  will react for the most part with its monomer  $M_1$ . Looking now at the AN-MEMOL system, the curve indicates the presence of an azeotropic mixture of monomers with a

content of 62 mol. % MEMOL. The relative reactivity of the MEMOL  $1/r_1$  with respect to the MMA radical is lower than with respect to the AN radical, while the reactivity of the MEMOL radical is greater with respect to the MMA than to the N. The product of  $r_1 \cdot r_2$  points to a greater tendency to alternation of the individual units and a more ordered structure in the MEMOL-AN copolymer.

Table 5. Copolymerization constants

$M_1$	$M_2$	$r_1$	$r_2$	$r_1 \cdot r_2$	$\frac{1}{r_1}$	$\frac{1}{r_2}$
AH	МЭМОЛ	$0,35 \pm 0,05$	$0,60 \pm 0,07$	0,20	3,03	1,6
MMA	МЭМОЛ	$1,65 \pm 0,13$	$0,50 \pm 0,07$	0,82	0,60	2

We then computed  $Q$  and  $e$  on the basis of values established experimentally for the MMA-MEMOL copolymerization constants. For MEMOL  $Q = 0.38$ ;  $e = -0.04$ . This enabled us to compute the copolymerization constants in accordance with the formulas of Alfrey and Price for the AN-MEMOL monomer pair ( $r_1 = 0.35$ ,  $r_2 = 0.60$ ), which are found to be in good agreement with the values of  $r_1$  and  $r_2$  for this pair as established experimentally. The values of  $Q$  and  $e$  for MMA and AN have been taken from the literature [5, 6].

It follows from the data in Table 1 that by copolymerizing AN and MEMOL we can produce copolymers with  $[\eta] = 1.5-2$  (in dimethylformamide). The properties of the copolymer will vary as functions of composition. When the content of the ester units in the copolymer is increased to 15-20 mol. %, it begins to be soluble in acetone, methyl ethyl ketone and dioxane.

### Conclusions

Copolymers containing butyric, acetic and benzoic esters of methyloylmetacrylamide and methylmethacrylate and acrylonitrile have been produced and a number of the properties of these materials analyzed. It has been shown that when the content of the ester units in the copolymers is increased to 15-20%, these materials begin to become soluble in acetone, methyl ethyl ketone and dioxane.

The constants for the copolymerization of the butyric ester of methyloylmetacrylamide and methyl methacrylate and acrylonitrile and values of  $Q$  and  $e$  for the butyric ester of methyloylmetacrylamide have been computed.

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