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Complex-radical copolymerization of vinylcyclohexyl ketones with maleic anhydride and N-p-tolylmaleimide

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Abstract

Some features of the formation and photochemical reactions of cyclohexylketone containing macromolecules including copolymers of vinylcyclohexyl ketone (VCHK) and its derivatives (V-α-Cl-CHK and V-δ-C1-CHK) with maleic anhydride (MA) and N-p-tolylmaleimide (TMI) have been revealed. It has been established that keto-enol tautomerism is the only reaction realized in the vinylcyclohexylketone molecules having mobile hydrogen atom at α -position in the cyclohexane ring, enol form of which is formed by charge-transfer complexes with anhydride or imide of maleic acid as acceptor monomers. The kinetic parameters of these reactions, including complex-formation and copolymerization constants, as well as the ratios of chain growth rates for the participation of monomeric charge-transfer complexes and free monomers, are all determined. It is shown that an alternative copolymerization is realized with the monomer systems containing VCHK and V- δ -C1-CHK, which are carried out through a complex-mechanism due to the keto-enol tautomerism; while random copolymer enriched with vinyl ketone units is formed with the system containing oc-substituted VCHK. It is found that characteristics of photochemical reactions of alternating copolymer synthesized depend on the type of substitutation in the vinyl ketone molecule; unlink VCHK-MA(TMI) and V-δ-C1-CHK-MA(TMI) copolymers case which easily crosslink upon UV-irradiation, and the N-substituted derivatives of these copolymers which decompose under similar condition.

Introduction

Polymers and copolymers of vinyl ketones are of major interest in regards to the preparation of reactive and photosensitive polymer film-forming materials-resists for microelectronics with a broad set of commercially fine properties.

An important characteristic of carbonyl-containing organic compounds (such as aldehydes, ketones. ketoesters, etc.) is the unusual activity of α-hydrogen atoms on carbon atoms adjacent to the C=O group, and it is assumed that the tautomerism is the basis for the chemistry of these compounds. For simple monocarbonyl compounds such as acetaldehyde, acetone and cyclohexanone, the amout of enol form present at equilibrium is very small, i.e. in the rang of 0.00015 % and 1.2 % [1]. The activity of α-hydrogen atoms, and hence degree of tautomerism depends on the type of carbon atom (primary or secondary), solvents, PH of reaction phase, temperature, etc. The low keto-enol proton tautomerization in the acetaldehyde - vinyl alcohol (K=[enol]/[keto] ≈ 3.10^{-7} at 25°C) has been reported by Capon, et al [2]. By taking advantage of stabilizing electron donor-acceptor interactions the free radical copolymerization of enolic tautomer of acetaldehyde with maleic anhydride proved to be successful [3]. Investigation of these authors demonstrated that equimolar amounts of maleic anhydride and 0-D vinyl alcohol (D is deuterium) were consumed during the formation of polymer, suggesting that an alternating (1:1) copolymerization occurs.

The role of different types of tautomers as monomers and polymerization initiators including keto-enol tautomers in the reactions of macromolecules formation are summerized in certain reviews [4,5]. Vinyl monomers, such as α,β-unsaturated ketones, with a polymerizable tautomers exhibit the coexistance of the keto and enol forms, and their tautomeric equilibra shift with the organic solvent. It was

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shown that the keto and enol tautomers are expected to differ in their reactivity [6,7].

The vinylcyclohexyl ketones with the characteristic of coupling of the multiple bond with the carbonyl group belong to the class of typical electron acceptor monomers. Therefore, the assumption on the formation of donor-acceptor complexes with the participation of the ð-electrons of double bonds of the vinyl ketones (acceptor) and electron-acceptor monomers (maleic anhydride and its derivatives) can be ignored. However, a more detailed study of vinylcyclohexyl ketones structure and as the factors ensuring their conversion to the electron donor form helped to reveal new aspects of radical alternating copolymerization reactions [5,8,9].

In this study, the effect of charge-transfer complex formation (via a kefo-enol tautomerism) on the copolymerization reactivities and chain growth reactions in the vinyl- ä -chlorcyclohexyl ketone (V-δ-Cl-CHK)-maleic anhydride (MA), vinyl-α-chlor- cyclohexyl ketone (V-α-Cl-CHK)-MA and VCHK-N-p-tolylmaleimide (TMI) systems, as well as on the photochemical reactions of cyclohexylketone alternating copolymers, are examined and discussed.

Experimental part

Materials

The initial VCHK, V-α-Cl-CHK and V-δ-C1-CHK are synthesized by use of the known method [9], and all one purified by twice distillation in the presence of 0,01 % p-oxy-diphenylamine as inhibitor. They had following characteristics:

VCHK - b.p. 68°C/0,67 kPa, n_D^{20} - 1,4710, d_4^{20} = 0,9301;

V-α-Cl-CHK - b.p. 116°C/1,33 kPa, n_D^{20} = 1,4970, d_4^{20}- 1,0891;

V-δ-C1-CHK - b.p, 130°C/1,33 kPa, n_D^{20} = 1,4980, d_4^{20}- 1,1112.

MA is recrystallized from benzene and sublimed at 50°C/2,5 kPa and used immediately after its purification; m.p. 52.8°C.

TMI is synthesized by the known technique [10] and is purified by recrystallization from a mixture of benzene and n-hexane; m.p. 143-144°C.

The initiator, benzoyl peroxide (BP), is purified by reprecipation from the chloroform solution with methanol.

Copolymerization

Reactions are carried out in methyl ethyl ketone (MEK) under the nitrogen atmosphere in the presence of BP at 50-80°C to conversions of 5-10 %. The copolymers produced are recovered by addition of a 10-fold excess of methanol and purified twice by reprecipation from benzene solution into n-heptane or methanol and by washing with some portions of diethyl ether. Purified copolymers are then dried in vacuo at 40°C to constant weight; copolymers synthesized are dissolved in polar and aromatic solvents. Copolymers synthesized by using equimolar composition of initial monomers had following characteristics:

VCHK-TMI alternating copolymer: softening point 147-150°C, [η] (benzene at 25^0C) 0,11 dL/g, N:4,27%.

FTIR (film): 3070-3035 ($\nu_{CH=}$ in tolyl ring), 2930-2862 (ν_{CH2}), 1778 ($\nu_{C=O}$ in cyclic imide), 1710 ($\nu_{C=O}$ of ketone), 1600-1505 ($\nu_{C=C}$ of aromatic ring), 1460 (δ_{CH2} in cyclohexyl ring), 1385-1290 (ν_{C-N}), 1195-1080 (δ_{CH}), 995-1030 cm^{-1} ($\nu_{C=C}$).

V-δ-Cl-CHK-MA alternating copolymer: softening point 117-120°C, [η] (benzene at 25°C) 0.12 dL/g, acid number 414 mg KOH/g, Cl: 13.15 %.

FTIR (film): 2930-2860 (ν_{CH2}), 1845 and 1775 ($\nu_{C=O}$ of anhydride ring), 1705 ($\nu_{C=O}$ of ketone), 1450 (δ_{CH2} in cyclohexyl ring), 1380-1045 (ν_{C-O-C}), 1150 (ν_{C-O}), 740 and 695cm^1(ν_{C-Cl}).

V-α-Cl-CHK-MA random copolymer: softening point 102-105°C, [η] (benzene at 25°C) 0.17 dL/g, acid number 212 mg KOH/g, Cl: 16.73 %.

FTIR spectra of this copolymer have similar peaks as in spectra of V-δ-C1-CHK-MA copolymer.

Copolymer analysis

Copolymer compositions were calculated from elemental (contents of Cl and N) and chemical analyses (by potentiometric titration of anhydride unit).

Fourier transformation infrared spectra were recorded with a FTIR Nicolet 510 spectrometer. ^{1}H NMR spectra were recorded with a AC-80 Bruker spectrometer at 25-45°C with deutered acetone and tetramethylsilane as solvent and internal standard, respectively. For the determination of

charge transfer complex (CTC) formation constants (K_C), the ^1H NMR method of Hanna-Ashbaugh [11] was used.

Kinetic studies ofcopolymerization were accomplished dilatometrically.

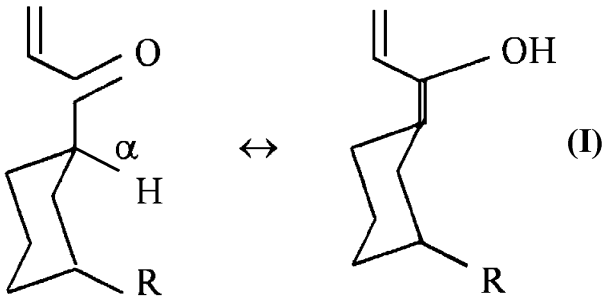
The copolymerization constants (r_1, r_2, r_{1C}, r_{1C1} and r_{1C2}) were determined simultaneously by using the terminal model of Kelen-Tüdös [12] as well as the complex model of Seiner-Litt [13].

Photochemical reactions of copolymers were studied by FTIR spectroscopically by using of a Osram-Ultra Vitalux E27 modernate pressure UV lamp (300 W) as a source of UV-irradiation.

Results and discussion

Keto-enol tantomensm

Cyclohexane derivatives of vinyl ketones can have a keto-enol tautomerism, which is attributable to the highly labile nature of the hydrogen atom in the α-positionof the ring



(I)

where R-H and/or Cl.

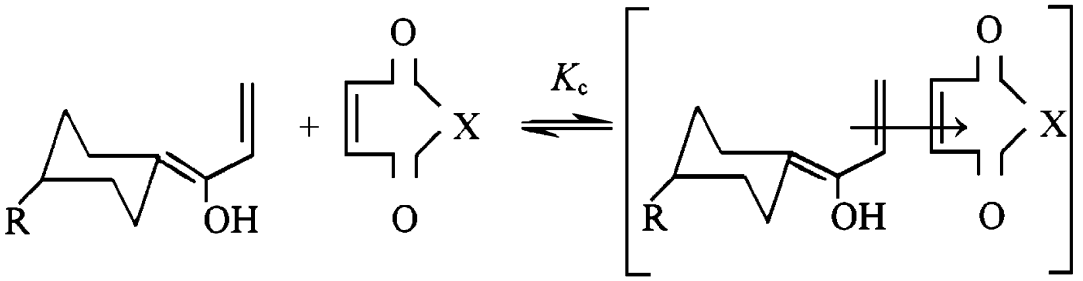
Naturally it can be considered that the keto-enol tautomerism ends completely in the case of substitution of the hydrogen atom in the ex-position on the chlorine atom.

FTIR spectra of the vinyl ketones studied show low intensity bands in the form of doublets in the 3630 and 3550 cm^{-1} regions which are associated with intermolecular and intramolecular

(Cl...HO)-bound OH groups. Due to the mobility of the hydrogen atom in the α-position of the cycle; the VCHK or V-δ-C1-CHK molecule is in the equilibrium state of the keto and enol forms as a result of which a weak doublet in FTIR being characteristic of the molecular bound hydroxyl group. The absorption band at 1620 cm^{-1} corresponds to the C=C bond and the peaks at 1680 and 1700^{cm-1} with different intensities characterize the absorption of the carbonyl groups present in the tram and cis positions in relation to the conjugated multiple bond, respectively. In the usual ^1H NMR spectrum the enol form of the vinyl ketones studied does not show up because of the overlap by its powerful and complex signals from the protons of the cyclohexane ring. Therefore, as was shown in our previous work [5] to detect it the paramagnetic reagent *Eu(fod)₂* (partially fluorinated ligand 1,1,1,2,2,3,3-heptafluoro- 7,7-dimethyl-4,6-octanedione) is necessary. As expected introduction of *Eu(fod)₂* leads to heavy shift of the proton of the enol form to the weak field with appreciable widening of the resonance line (3.1-3.4 ppm). It may be assumed that the C=O groups of the *trans-S*-form undergo enol conversion, since in the case of the *cis-S*-conformation such a transition is less advantageous energetically.

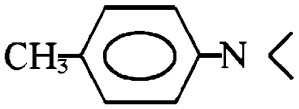
Charge transfer complex formation

The formation of CTC between the VCHK's and MA (or TMI) was substantiated by the results of ^1H-NMR analysis of the spectra of the pure monomers and their mixtures at different ratios. From the structural peculiarities of the studied VCHK's containing two polymerizable keto and enol tautomers one can predict that the formation of an equimolecular (1:1) CTC in the monomer systems VCHK's (enol form)-MA(or imide) which proceeds as following:



(II)

(enol form) *(CT-Complex)*

were R = H and Cl; X = −O− and 

Equilibrium constants of 1:1 complex (Kc) between V-δ-C1-CHK (enol form) and MA as well as Kc for VCHK...TMI complex were determined by using of ^{1}H NMR spectral data (Fig. 1 and Table I) and the well known Hanna-Ashbaugh equation [11].

The concentration of acceptor monomer (*A*= MA and TMI) in different mixtures with donor monomers (D = VCHK's) were kept constant at 0.1 mol/L, while the concentrations of MA and TMI acceptor monomers were increased, i.e., [D]>> [*A*]. The appreciable displacement of chemical shifts observed for anhydride (δ^f == 7.34 ppm) and imide (δ^f = 6.95 ppm) protons into the strong fields with significant excesses of donor monomers ($\Delta_{exp} = \delta^f - \delta^c$ = 0.007-0.04 ppm) allows one to determine the values of K_c from the graphical relationship of $1/\Delta_{exp} \rightarrow 1/[D]$ (Fig. 2). Unlike the well known monomeric donor-acceptor complexes, where increase of temperature is expected to decrease the Kc values in this study, increase of temperature led to increase of their values, for the monomer systems studied. The observed anomaly may be explained by increase in the fraction of the enol form of the vinyl ketones with increase in temperature. Equilibrium constant for V-α-CI-CHK...MA complex is found as Kc → 0 (Fig. 2) which is indicated that because of the absence of mobile hydrogen atom in a-position cyclohexane ring, keto-enol tautomerism does not proceed in the V-α-C1-HK...MA system.

The results of measurement of Kc values at a series of different temperatures were illustrated in Table I. These data allow one to determine of the activation energy (E_a) for complex formation Reaction proceeding via a keto-enol tautomerism.

The values of E_a calculated (Fig. 3) are found to be 1.47 kJ / mol (for for V-δ-C1-CHK...MA complex) and 3,98 kJ / mol (for VCHK...TMI complex). These values of E_a can also be used for characterization of enolization reaction of vinyl ketones studied in the presence of acceptor monomers (MA or TMI). The considerable lowering of the Kc value and high E_a value for VCHK. ,TMI complex in comparison with V-δ-CI-CHK...MA as well as with VCHK...MA complex with Kc - 0.05 [8] is evidently connected with the weaker electron-acceptor strength of TMI. On the other hand, the arrangement in space of the comonomer molecules in space gave maximum molecular orbital overlap of the vinyl group of VCHK and of the benzene ring of TMI which lead to a larger distance between the double bonds and evidently may also result in weakening of complex formation. With the disappearance of the conjugation between the multiple bond and the carbonyl group, the vinyl group of the enol form is characterized by higher electron density due to which VCHK and its derivatives are capable of forming CTC with anhydride and imides of maleic acid belonging to monomers of the acceptor type.

From the experimental findings and the structural features of the VCHK's; it may be assumed that, the keto-enol tautomerism is due to the high mobility of the hydrogen atom in the a-position of the cycle and they form part of the intermolecular complexes with the maleic acid derivatives in the enol form of the trans-S-conformation.

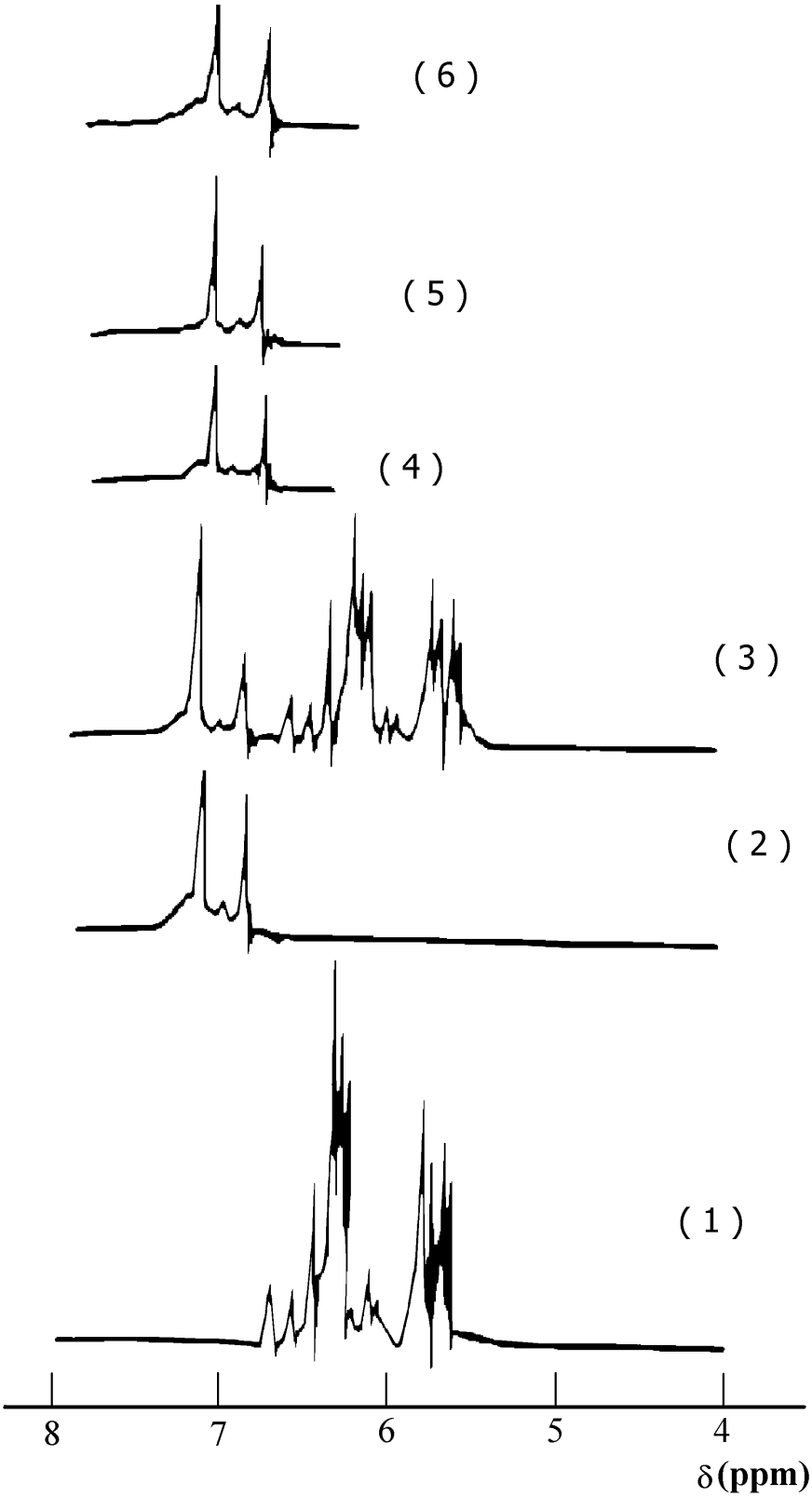


Fig. 1. ^{1}H NMR spectra of (1) VCHK and its mixtures with (2) TMI ar molar ratio of [imide] : [ketone] = 1:10 (3), 1:20 (4), 1:30 (5) and 1:50 (6). Sovent, CD_3–CO–CD_3, internal standard, $(CH_3)_4Si$, 35±0,1 ^{o}C .

Table 1

Effect of temperature in complex formation of VCHK's enol form as donor monomers (D) with MA and TMI as acceptor monomers (A)

[D] (mol/L)	[A] (mol/L)	T (°C)	δ(A) (pmm)	$*\Delta_{exp}$ (ppm)		*K*c (mor^{-1})
V-δ-C1-CHK-MA						
0.0	01		25	7340	00	
2.0	0 1		25	7325	0015	
30	01		25	7320	0020	0101001
40	01		25	7316	0024	
50	0 1		25	7308	0032	
20	01		35	7323	0017	
30	0 1		35	7318	0022	0151001
40	01		35	7315	0025	
50	0 1		35	7305	0035	
20	0 1		45	7318	0022	
30	0 1		45	7311	0029	018±002
40	0 1		45	7306	0034	
50	0 1		45	7300	0040	
VCHK-TMI						
00	0 1		25	6950	00	
3 3	0 1		25	6943	0007	
40	0 1		25	6941	0009	0 019 ± 0002
50	0 1		25	6940	0010	
63	0 1		25	6937	0013	
22	0 1		35	6942	0008	
30	01		35	6941	0 009	0 028 ± 0 003
40	0 1		35	6928	0012	
56	0 1		35	6925	0019	
20	0 1		45	6941	0009	
30	0 1		45	6928	0012	0 038 ± 0004
40	0 1		45	6935	0015	
56	0 1		45	6923	0027	
V-α-CI-CHK-MA						
00	01		35	7340	00	
20	01		35	7337	00029	
30	0 1		35	7335	00047	0 0061±0 0005
40	01		35	7334	00055	
50	01		35	7333	00071	

$*\Delta_{exp} = \delta(A) - \delta(A\ldots D)$

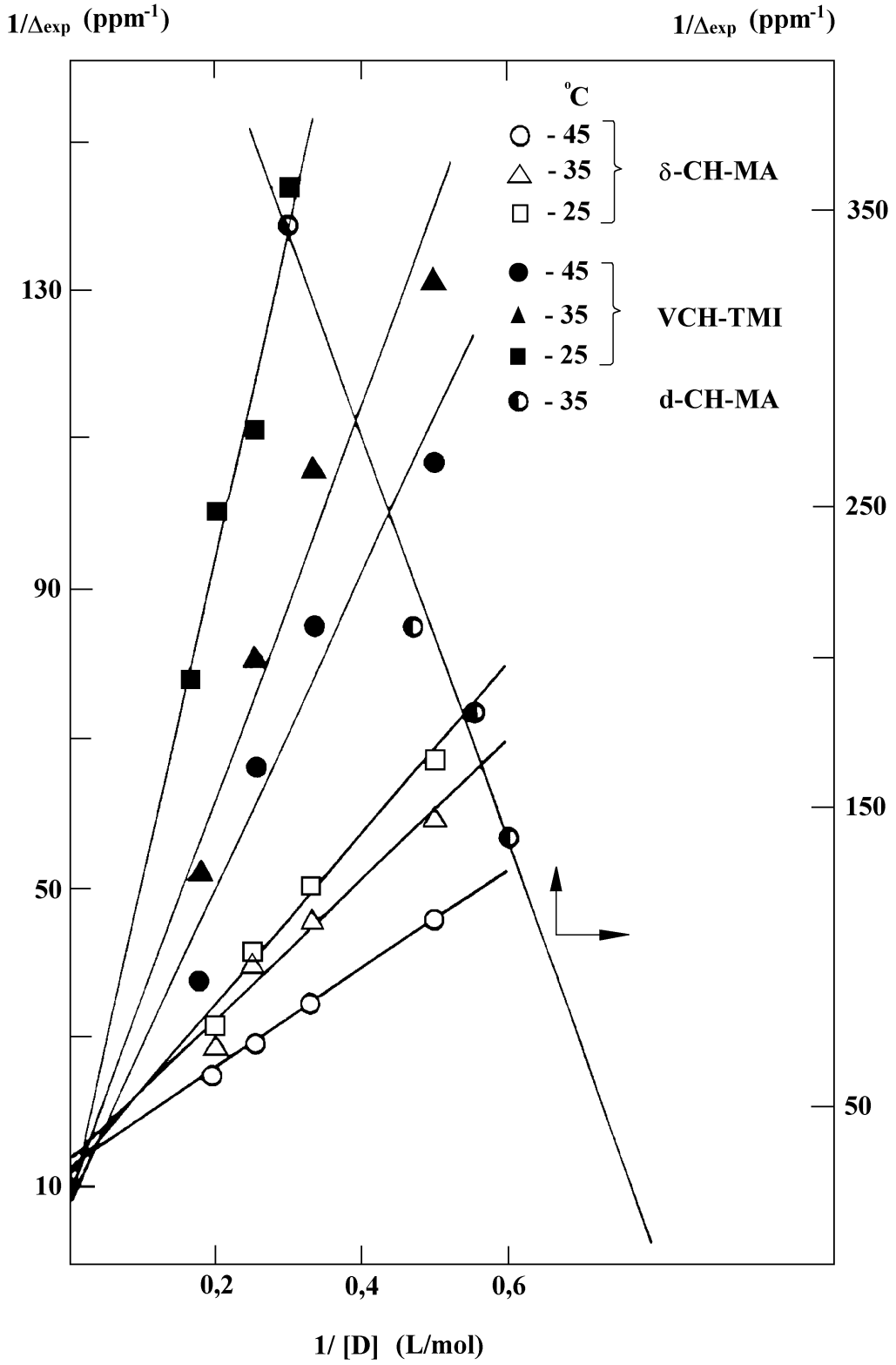


Fig.2. Graphic determination of K_c constants for V–δ–Cl–CHK…MA (–o–, 45°C, –Δ–, 35°C, –□–, 25°C) V–α–Cl–CHK…MA (–o–, 35°C) and VCHK…TMI (–•–,45°C, –Δ–, 35°C, –□–, 25°C) charge tranfer complexes. $1/\Delta_c$ is *y*-axis, $Tg\alpha = 1/\Delta_c K_c$; $1/\Delta_{exp}$ is the difference between chemical shifts of MA and TMI protons and those in the mixtures of [D]>>[A].

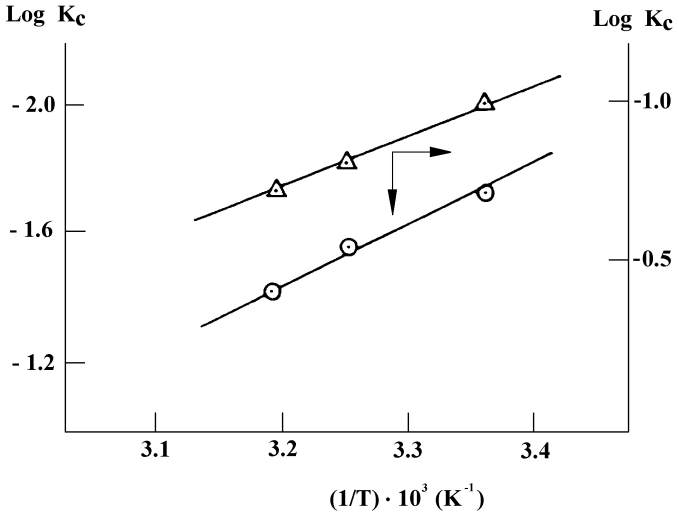


Fig.3. Arrhenius plot of CTC-formation via an enolization in V-δ-C1-CHK-MA (-o-) and VCGK-TMI (-Δ-) monomer systems.

Complex-radical copolymerization

It is known that vinylphenyl(methyl) ketones enter into radical copolymerization reaction with MA. However, it appears that [14] no alternating copolymerization takes place, and that random copolymers enriched with vinyl ketone units are formed. Despite this, when cyclohexyl derivatives of vinyl ketones were copolymerized it was found that regularly alternating copolymers of 1:1 composition were obtained; In addition, a study is made for the quantitative contribution of monomeric CTC to radical reactions of chain propagation [5]. Table 2 shows the monomer-copolymer composition relationships. It is seen that, V-δ-C1-CHK-MA and VCHK-TM1 copolymers are both close to an equimolar composition, being irrespective of composition of the initial monomer mixture used. These relationships break for the V-α-Cl-CHK-MA system; increase of vinylketone concentration in initial monomer mixture lead to a monotoneous growth of the ketone ring fractions in the random copolymers formed.Copolymerization of VCHK's (M_1) used with MA (or TMI) as an acceptor monomer (A) can be characterized by the following intermolecular reaction scheme including chain growth; allowing for free and complex-bound monomer:

Keto-enol tautomerism

$$M_1\ (\textit{keto}\text{-form}) \underset{}{\overset{k_t}{\longleftrightarrow}} M_1\ (\textit{enol}\text{-form}) \qquad (1)$$

CTC formation

$$M_1\ (\textit{enol}\text{-form}) + A \underset{}{\overset{K_c}{\longleftrightarrow}} [M_1\ (\textit{enol}\text{-form})\ldots A] \qquad (2)$$

Propagation reactions

$$\sim M^{\bullet}_1 + A \overset{k_{12}}{\rightarrow} \sim A^{\bullet} \qquad (3)$$

$$\sim M^{\bullet}_1 + M_1 \overset{k_{11}}{\rightarrow} \sim M^{\bullet}_1 \qquad (4)$$

$$\sim A^{\bullet} + M_1 \overset{k_{21}}{\rightarrow} \sim M^{\bullet}_1 \qquad (5)$$

$$\sim M^{\bullet}_1 + A\ldots M_1 \overset{k_{1c}}{\rightarrow} \sim M^{\bullet}_1 \qquad (6)$$

$$\sim A^{\bullet} + M_1\ldots A \overset{k_{2c}}{\rightarrow} \sim A^{\bullet} \qquad (7)$$

Table 2
Copolymerization of VCHK and its α-Cl- and δ-Cl-substituted (M_1) with MA and TMI (M_2). Reaction conditions: solvent, MEK; 60°C; initiator, [BP] 1.57 x 10^{-3} mol l^{-1}; [M] = 1.0 mol l^{-1}; conversion ≤ 10 %

Monomer mixture (mol %)		AN (mg KOH g^{-1})	Analysis (%)	Copolymer composition♦ (mol %)		P ar ameters of equations			
						KT-eq		SL-eq	
$[M_1]$	$[M_2]$		C1(N*)	m_1	m_2	$\xi x10^2$	$\eta x10^2$	χxlO^2	$(y-1)xl0^2$
VCHK-TMI									
30	70	-	4.48	47.64	52.36	17.32	-3.65	33.94	-9.88
40	60	-	4.38	48.91	51.09	32.52	-2.08	22.37	2.85
50	50	-	4.27	50.45	49.55	50.47	0.92	17.84	3.65
60	40	-	4.03	53.72	46.28	66.79	7.16	98.29	11.09
70	30	-	3.92	55.21	44.79	82.68	6.52	97.15	21.60
V-δ-C1-CHK-MA									
30	70	446	12.52	47.06	52.94	17.85	-4.63	19.75	-10.08
40	60	416	13.07	49.87	50.13	32.93	-2.38	13.53	-0.44
50	50	414	13.15	50.15	49.85	51.10	0.31	9.76	9.21
60	40	386	13.61	52.77	47.23	67.92	5.31	7.08	20.97
70	30	359	14.10	55.44	44.56	82.15	8.60	4.73	38.31
V-α-Cl-CHK-MA									
30	70	321	14.77	59.30	40.70	25.01	26.66	-	-
40	60	284	15.82	65.58	34.42	38.16	51.82	-	-
50	50	212	16.73	71.43	28.57	51.41	77.12	-	-
60	40	165	17.57	77.12	22.88	63.84	100.91	-	-
70	30	121	18.35	82.77	17.23	74.99	122.25	-	-

* Contents of N in VCHK-TMI copolymer
♦ Calculated for alternating copolymers: N 4.30 % for VCHK-TMI copolymer; Cl 13.10 % and AN 414.5 mg KOH g^{-1} for V-δ-C1-CHK-MA copolymer

The copolymerization constants for the monomer pair systems studied were calculated using the data of Table 2 and the terminal model equations of Kelen-Tüdös (KT),[12] equation (8), as well as the terminal complex model equation of Seiner-Litt (SL),[13] equation (9),

$$\eta = (r_1 + r_2/\alpha)\,\xi - r_2/\alpha \qquad (8)$$

$$(y-1) = r_{1c}/r_{1c1} + (r_{1c}/K_c)\,\chi \qquad (9)$$

where $F = [M_1]/[M_2]$, $f = m_1/m_2$, $\eta = (F^2/f)/(\alpha + F^2/f)$, $\xi = [F(f-1)/f]/(\alpha + F^2/f)$, $\alpha = \sqrt{(F2/f)\min \times (F2/f)\max}$, $y = (1 + r_{12}F)/(1 + r_{21}F^1)$, $\chi = 1/[M_2]\,[1 - (y-1)/r_{12}F]$, $r_{1c} = (r_{1c1} + r_{1c2})/(r_{1c1} \times r_{1c2})$ for the condition of $k_{1c} = k_{1c1} + k_{1c2}$.

The copolymerization constants of both free and complex-bound monomers calculated from data of Table 2 were found to be: $r_1 = 0.186 \pm 0.015$ and $r_2 = 0.086 \pm 0.005$ (by KT-eq.); $r_{1c} = 0.45$, $r_{1c1} = 1.01$ and $r_{1c2} = 0.82$ (by SL-eq.) for V-δ-C1-CHK-MA system; $r_1 = 0.054 \pm 0.002$ and $r_2 = 0.108 \pm 0.01$ (by KT-eq.); $r_{1c} = 0.025$, $r_{1c1} = 0.12$ and $r_{1c2} = 0.032$ (by SL-eq.) for VCHK-TM1 system; $r_1 = 1.70 \pm 0.15$ and $r_2 = 0.08 \pm 0.005$ (by KT-eq.) for V-α-Cl-CHK-

MA system. As evidenced from these values, alternating copolymerizations are realized in the V-δ-C1-CHK-MA and VCHK-TMI systems; while random copolymerization is proceeded in the V-α-Cl-CHK-MA system. In this connection the SL - equation, is applied to the system studied where one of the monomers is not viable to homopolymerization, enables one to find the ratios of the rate constants of attachment of free monomers and CTC to homonymous macroradicals as well as to demonstrate the considerable by several orders rise in the reactivity of CTC as compared with that of free monomers.

From measurements of the initial rates of copolymerization for the equimolar monomer feed of V-δ-C1-CHK-MA and VCHK-TMI in MEK at 60°C and at various selected overall monomer and initiator (BP) concentrations; general kinetic equations of copolymerization for both systems are obtained. The kinetic order with respect to BP (n) and monomers (m) calculated from data of Fig. 4a and 4b were found to be n = 0.50 and 0.52, and m = 1.9 and 1.2 for V-δ-C1-CHK-MA and VCHK-TMI pairs, respectively. By using these values, the following copolymerization equation obtained have yielded (R_p - k^{60} $[BP]^n$ $[M]^m$) the copolymerization rate constants at 60°C for equimolar feed case: k^{60}=0,49×10^{-5} L/mol.s and k^{60}=4.5×10^{-5} L/mol.s for V-δ-C1-CHK-MA and VCHK-TMI systems, respectively.

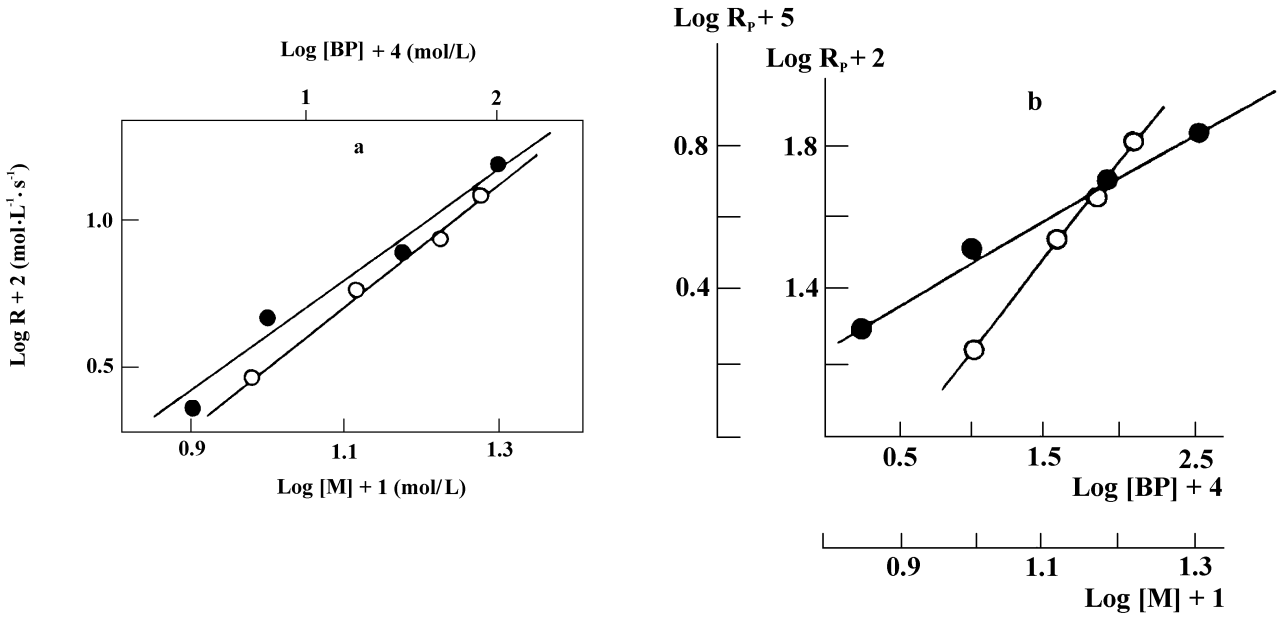


Fig.4. Plots of copolymerization rate vs. concentration of initiator, [BP] (-•-) and overall monomer concentration, [M] (-o-) for V-δ-C1-CHK-MA *(a)* and VCHK-TMI *(b)* monomer systems.

The dependency of initial copolymerization rate (R_p) on the monomer compositions at different total monomer concentrations for V-δ-C1-CHK-MA and VCHK-TMI systems, respectively, are plotted in Fig. 5a and 5b, recpectively. It is shown that there is a characteristic maximum, and on dilution; R_p maxima shifts (at ~ 40-55 mol % of MA or TMI) towards reduced VCHK's. By the kinetic method [8] "shift of rate maximum", participation of donor-acceptor complexes in the chain growth reaction could be quantitatively determined. Changes observed in the position of the maxima accompanying a reduction in the total concentration of monomers is attributable to both free monomers and complex-bound monomers participating in chain growth reactions. Results of kinetic study (Fig. 5) and use related equations [8] allows one to evaluate the quantitative contribution of complexes to propagation reactions as well as

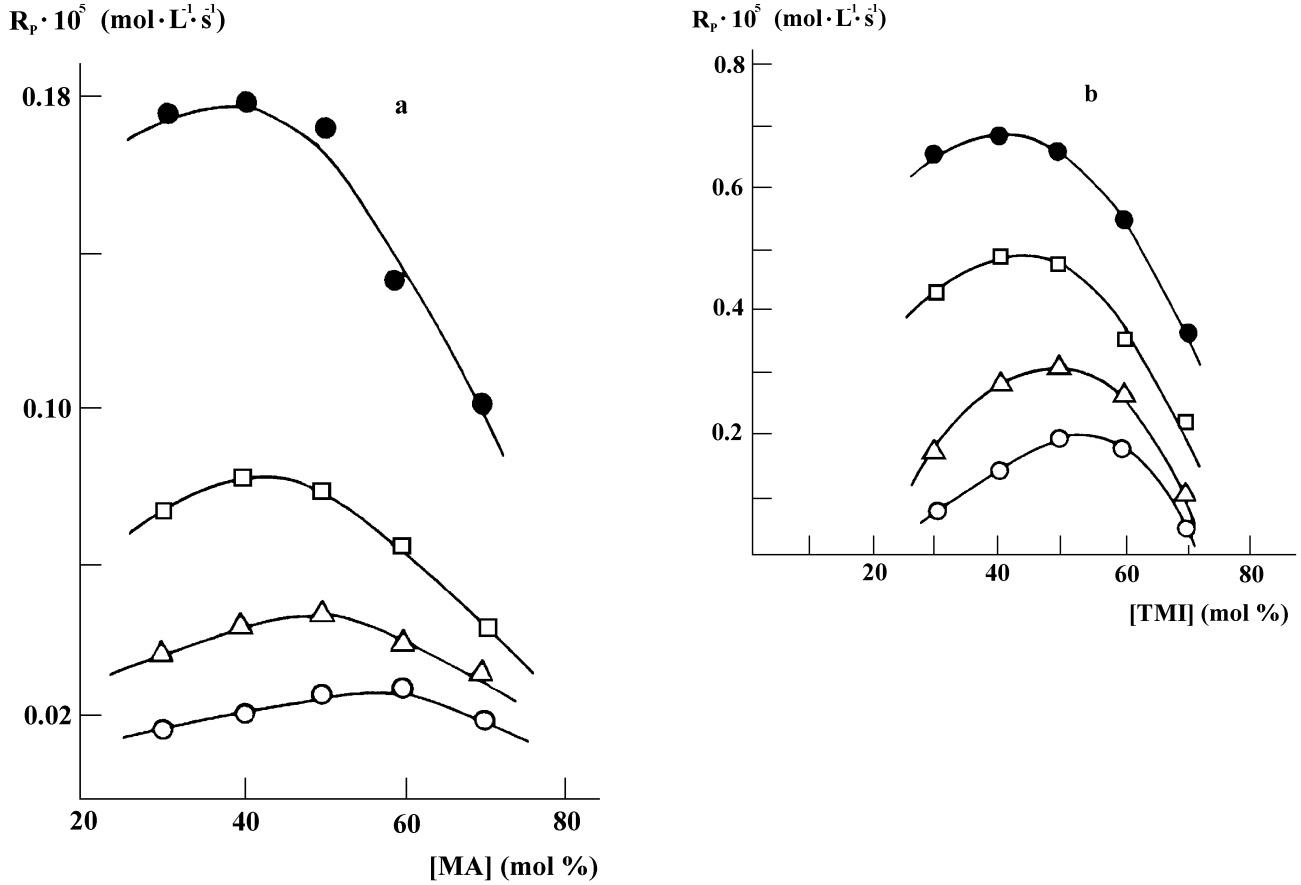


Fig.5. Plots for V-δ-C1-CHK-MA *(a)* and VCHK-TMI (b) copolymerization rates vs. monomer composition and overall concentration of monomers. Solvent, MEK; 60 ± 0.1°C; [BP] 1.57 x 10^{-3} mol l^{-1}; [M] = 0.75 (-o-), 1.0 (-Δ-), 1.5 (-□-) and 2.0 mol l^{-1} (-•-).

ratios of cross-propagation rate constants: k_{1c}/k_{12}= 6.04, k_{2c}/k_{21} = 2.83 and k_{21}/k_{12} = 3.4 for V-δ-C1-CHK-MA; k_{1c}/k_{12} = 16.2, k_{2c}/k_{21} = 2.2 and k_{21}/k_{12} = 1.97 for VCHK-TMI system. It follows from the value of k_{21}/k_{12} ratio that the reactivity of macroradical ~V-δ-Cl-CHK$^{\bullet}$ (or ~ VCHK$^{\bullet}$) with respect to acceptor monomers (A) is lower than that of ~A$^{\bullet}$ with respect to the vinyl ketone involved. The values k_{1c}/k_{12} and k_{2c}/k_{21} show that the existence of the complex with respect to ~A$^{\bullet}$ is many times more probable in compared with the macroradical with a ketone terminal unit. The ratios of rate constants of elementary steps (3), (5), (6) and (7) obtained suggest that the reactivity of the monomers increase when they are bound in complexes. It is shown that as the reaction system is diluted and the MA concentration in the monomer mixture increase, the probability of propagation through addition of the complex decrease on account of a reduction in the concentration of CTC's in the initial mixture. At the same time the position of R_{max} approximate to an equimolar monomer composition, which is due to increased probability of VCHK's transition to the enol form, which is responsible for a purely complex-based type of propagation mechanism. The values of k_{1c}/k_{12} and k_{2c}/k_{21} k_{21}/k_{12} ratios for these systems as well as for other systems including isostructural analogs of monomers studied are all shown in Table 3.

Kinetic study was also carried out for copolymerization of V-α-Cl-CHK with MA in similar conditions. The characteristics of curves in Fig. 6 show the linear dependency of R_p on V-α-Cl-CHK concentrations in V-α-Cl-CHK-MA system which can be considered as a typical random copolymerization reaction. In view of the results obtained it is concluded that regularly alternating chain propagation in the radical

Table 3

Ratios of the elementary growth reactions of complex-radical copolymerization ofVCHK's with anhydride (MA) and imides (TMI and phenylmaleimide, PMI)

Monomer pair	*K*c (l mol^{-1})	k_{1c}/k_{12}	k_{2c}/k_{21}	k_{21}/k_{12}
VCHK-MA [8]	0.075	10.95	3.64	6.59
V-δ-C1-CHK-MA	0.150	6.04	2.83	3.40
VCHK-PMI[9]	0.042	22.01	4.75	1.84
VCHK-TMI	0.028	16.20	2.20	1.97

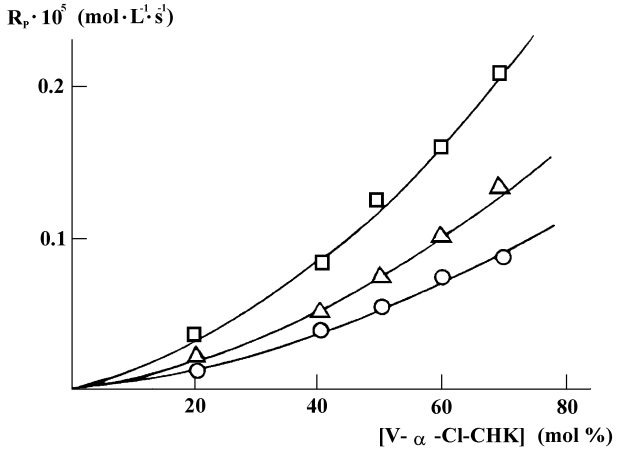


Fig.6. Plot for V-α-Cl-CHK-MA copolymerization rate vs. monomer composition and overall concentration of monomers. Conditions as in Fig. 5; [M] = 0.75 (-o-), 1.0 (-Δ-) and 1.5 mol l^{-1} (-□-).

copolymerization of VCHK's with MA and TM1 is due to transition of vinyl ketones molecule to an enol form, which favors formation of CTC with MA (or TMI), and take place by "mixed" mechanism with complex-bound monomers playing a dominant role. These results may be also interpreted with reference to the possibility of attachment of both complex-bound and free monomers to the growing macroradicals.

Photochemical Reactions

It is known that most functional macromolecules with carbonyl groups (ester and ketone type) in side chain, and alternating copolymers of mono- and bifunctional monomers (vinyl and allyl derivatives ofacrylic, maleic and cinnamic acids, etc) have a high sensitivity towards various type of irradiations such as UV, E-beams and X-rays [15-17] and their thin films or coatings have a wide range of use in microelectronics as resists of negative and positive type [18-22].

The photochemical reactions involved in thin alternating copolymer films obtained from their MEK solution by ultracentrifugation at different stages of UV irradiation are studied by FTIR spectroscopic method (Fig.7, spectra 2-4). The spectra of equimolar mono- mer mixture (Fig. 7, spectra 1) used as a model system. The characteristic and direction of photochemical reactions (photocrosslink or photodestruction) are estimated by the change of intensity of characteristic bands of functional groups.

Comparison of specta of equimolar monomer feed of V-δ-C1-CHK / MA and alternating copolymer, it is seen that the bands of anhydride and vinyl ketone C=C bonds (1640 and 1620 cm^{-1}) are absent in the spectra of copolymer, and simultaneously C=O band of ketone S-trans-conformer (1775 cm^{-1}) also disappeared. The following visible changes in the copolymer spectra are observed in the range of 1500-900 cm'^{1} after its UV exposition (1) first appearance (during 30 min irradiation) and increase (during 60 min irradiation) of 1650 cm^{-1} ($\nu_{C=C}$) and 1745 cm^{-1} ($\nu_{C=O}$, ester) band intensities; (2) decrease of ketone C=O band intensity in the range of 1705 and 1710 cm^{-1}, while a decrease in the anhydride characteristic band intensities ($\nu_{C=O}$, 1845, 1775 cm^{-1}). Moreover, essential decrease of C-Cl band intensities (740 and 695 cm^{-1}) is also observed which can be explained by partial dehydrochlorination of δ-C1-CHK ring during UV exposition of copolymer.

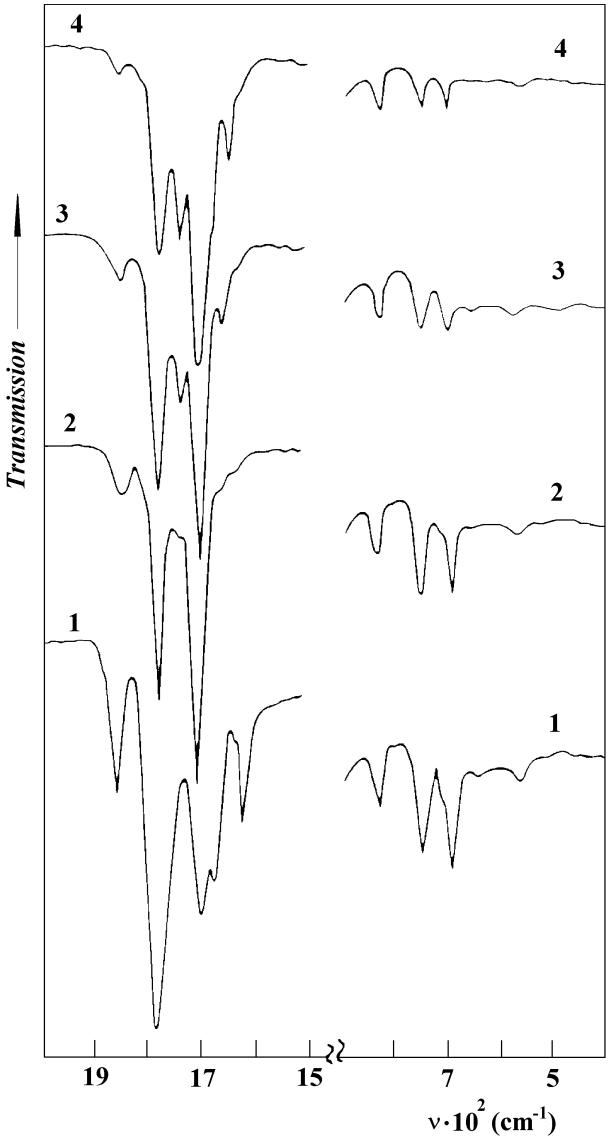


Figure 7. Fragments of FTIR spectra of equimolar V-δ-C1-CHK-MA monomer feed (1) and its alternating copolymer before (2) and after UV irradiation during 30 (3) and 60 min (4).

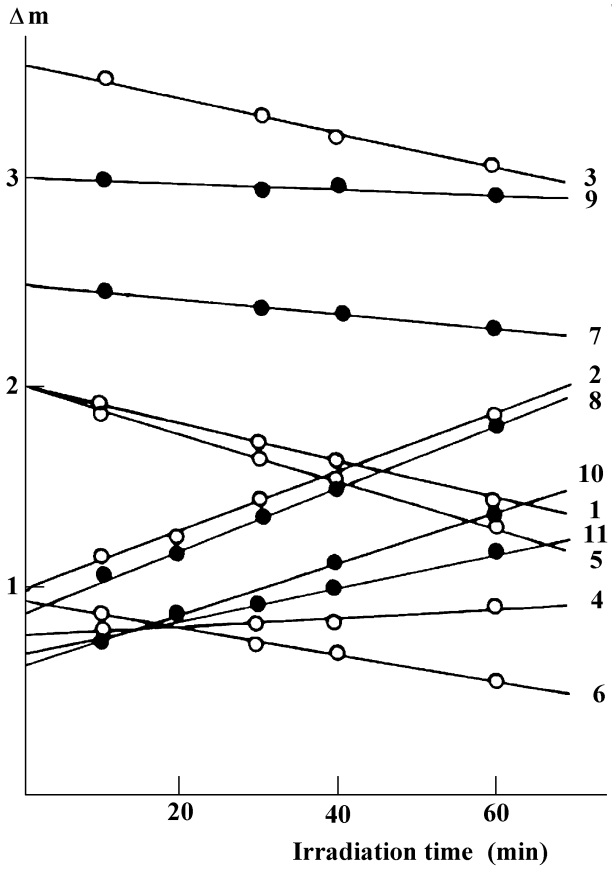
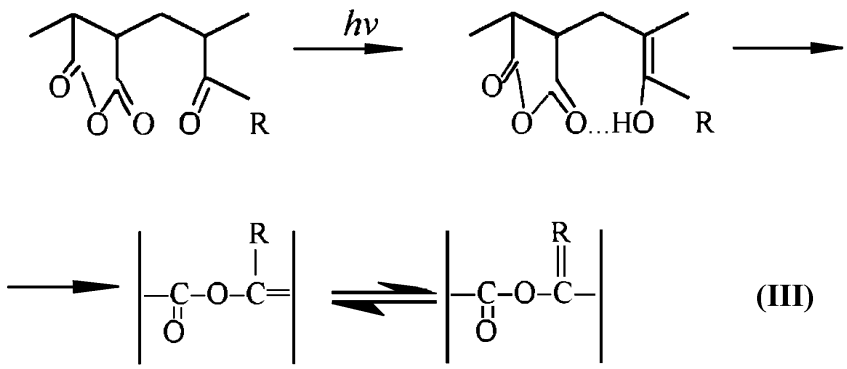


Figure 8. Plot of the absorpance change, Δm (1375) vs. UV-irradiation time for bending bands of V-δ-C1-CHK-MA (1-6) and VCHK-MA (7-11) copolymers: (1, 7) 2860, (2, 8) 1735, (3, 9) 1705, (4, 10) 1650, (5) 985, (6) 740, (11) 1200 cm^{-1}.

For a better illustration of the changes occuring in V-δ-C1-CHK-MA and VCHK-MA copolymer spectra with irradiation time, the difference between the absorption of bands after and before UV exposition is used. The intensity ratio between typical absorption bands and the least changing band (m^{1375}) is used to illustrate the changes in the spectra. The change Δm (m_o-m_t) at the initial irradiation stage can serve as a parameter characterizing photochemical conversions during absorption of irradiation energy. The results are shown in Fig. 8. As evidence from plots of Δm vs. Irradiation time, most dramatic changes are due to C=O (ketone and anhydride), C=C (in enol form and/or in cycle), CH_2 and C-C1 (cyclohexane ring) groups and bonds. The presence of Cl-substitute in macromolecules also speed up the photochemical conversion of copolymer.

The changes observed in FTIR spectra and also changes connecting with the brakes of rotation, vibration and segmental flexibility of main

and side chain bonds and groups of macromolecules (general decrease of all band intensities) as well as transfer of initial soluble thin films to insoluble form after UV irradiation allow to propose thatthe photochemical reactions of V-δ-C1-CHK-MA alternating copolymer dominantly proceed in direction of cross-linking of macromolecules with formation of cross-ester fragments through an intermediary enolization by the following overall scheme:



(III)

Where R = cyclohexyl and δ-chlorcyclohexyl.

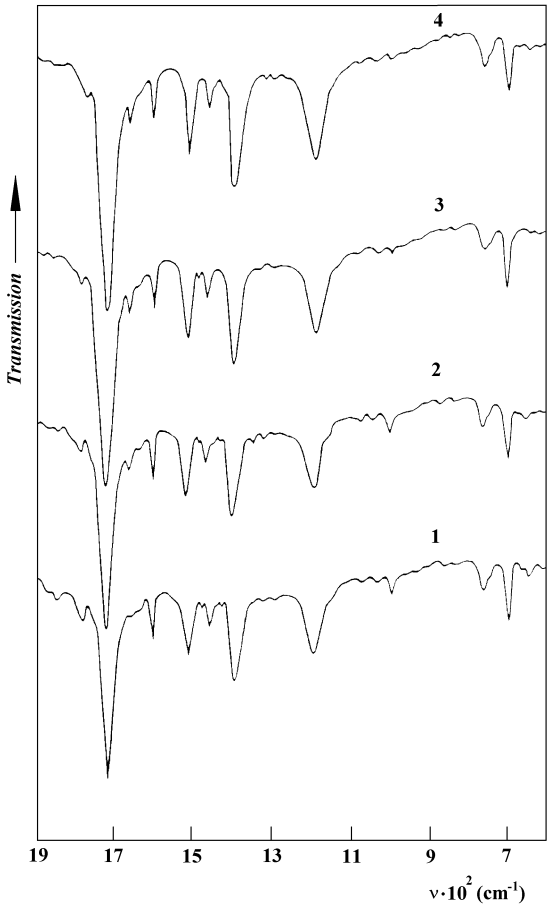


Fig.9. FTIR spectra of equimolar VCHK-TMI alternating copolymer before (1) and after UV irradiation during 15(2), 30(3) and 60 min (4).

Unlike anhydride copolymer used, the VCHK-TMI imide alternating copolymer primarily undergo to photodestruction reactions in the analogous conditions of UV irradiation. This fact is confirmed further by their good solubility of exposed copolymer films in organic solvents and by increase of most of characteristic bands (Fig. 9) connecting with increase of functional fragment flexibility of macromolecules.

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