

Kinetic Features and Molecular-Weight Characteristics of Terpolymerization Products of the Systems Based on Vinyl Acetate and 2-*tert*-Butyl-peroxy-2-methyl-5-hexene-3-yne

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ABSTRACT: Investigations of terpolymerization kinetics of the system on the basis of vinyl acetate (VA), peroxidic monomer (VEP) 2-*tert*-butyl-peroxy-2-methyl-5-hexene-3-yne, and acrylic acid proved that it falls under the equation of faintly inhibited copolymerization in which VEP serves as a comonomer and a chain-transfer agent. The contribution of each stage to the summary process rate is defined by the monomer ratio and depends on their consumption rate. Combination of a low-active VA monomer and of a VEP faint inhibitor in the system allows the control of the Trommsdorf effect and molecular-weight characteristics of functional oligoperoxides by changing the component ratio. The new carbon chain oligomers containing ditertiary alkyl peroxide and polar functional groups have practical application as multicenter surface-active radical initiators of polymerization and structurization. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1061–1066, 1998

Key words: peroxidic monomer; terpolymerization; kinetics; molecular-weight characteristics

INTRODUCTION

The promoting influence of maleic anhydride (MA) and acrylic acid (AAc) on the copolymerization of the systems including low active monomers is well known.¹ The introduction of active comonomers (MA and AAc) into a vinyl acetate (VA) and 2-*tert*-butyl-peroxy-2-methyl-5-hexene-3-yne (VEP) binary system results in a copolymerization rate increase and in the anticipated peroxide-containing copolymer yield.²

At the same time, VEP participation in the reaction of chain propagation as well as in transfer and termination reactions by a radical-induced decomposition mechanism³ determines some special features of such monomer system polymerization kinetics. This work is devoted to a theoretical

and experimental analysis of the influence of unsaturated peroxide participating in all radical polymerization elementary stages on the kinetic features and on the molecular-weight characteristics of the terpolymerization products.

EXPERIMENTAL

VEP ($\text{CH}_2=\text{CH}-\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)_2-\text{O} : \text{O}-\text{C}(\text{CH}_3)_3$) had the following characteristics after vacuum distillation: $d_4^{20} = 0.867$ (refer. 0.867); $n_{20}^D = 1.4480$ (refer. 1.4482); active oxygen content was 8.79% (Calcd. 8.75%). VA was purified by double-column distillation at atmospheric pressure; AAc was purified under vacuum. After that, their constants conformed to reference data.⁴ Benzoyl peroxide (BP) and dinitrile of azobisisobutyric acid (AIBN) were purified by recrystallization from ethanol. Dimethyl formamide (DMF)

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and methanol were dried and purified by a conventional technique.⁵

Terpolymerization was carried out in DMF with BP initiator or in methanol medium with AIBN initiator in argon atmosphere at 353 and 343 K, respectively. Monomer conversion was monitored by dilatometric and gravimetric methods. The rates were defined by linear section incline of conversion versus time dependence curve up to 7–10% conversion degree for each monomer ratio. Copolymers were purified by double precipitation from acetone solution to light petroleum and were dried under vacuum to constant weight.

Terpolymer compositions were determined by physical and physicochemical methods. The error of functional group determination did not exceed 5–7%. Molecular-weight distribution (MWD) parameters were studied by a gel permeation chromatography method with a "Waters Co." gas-liquid chromatograph. Tetrahydrofuran was the eluent, its flow rate was 1.2 mL/minute, and the temperature was 298°K. The column calibration technique and the calculation of M_N , M_W , and M_Z values and their ratios were described in a previous work.⁶

RESULTS AND DISCUSSION

Experimental dependencies of VA, VEP, and AAc terpolymerization rates versus VEP relative con-

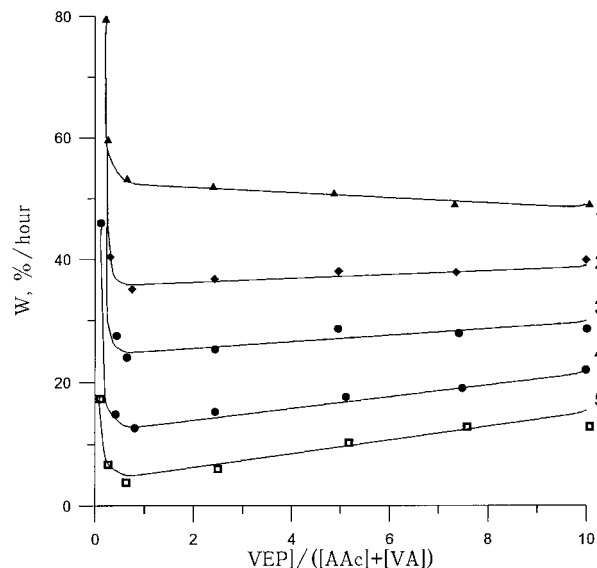


Figure 1 Dependence of VA, VEP, and AAc terpolymerization rate (W) versus $[VEP]/([VA] + [AAc])$ mole ratio at $[AAc]/[VA] = (1) 1.00, (2) 0.75, (3) 0.50, (4) 0.25, \text{ and } (5) 0.10$; (343 K, methanol, $[AIBN] = 3 \times 10^{-2} \text{ kmol/m}^3$, monomer mixture concentration $[C_m] = 4 \text{ kmol/m}^3$).

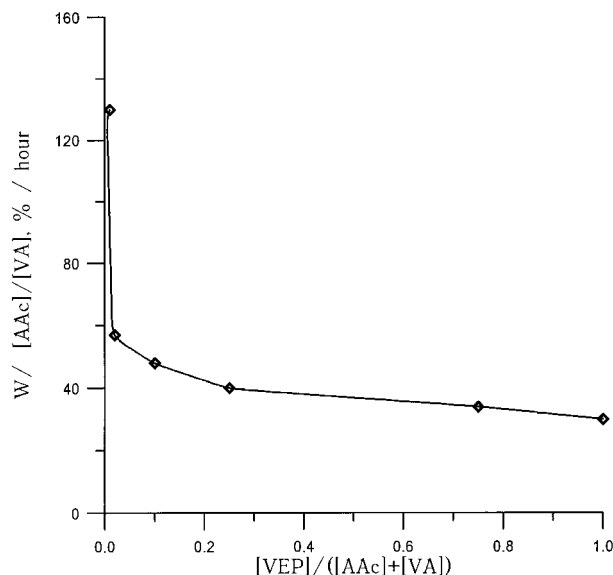


Figure 2 Dependence of terpolymerization relative rate versus $[VEP]/([VA] + [AAc])$ mole ratio; (343 K, methanol, $[AIBN] = 3 \times 10^{-2} \text{ kmol/m}^3$, $C_m = 4 \text{ kmol/m}^3$).

tent in the reaction mixture are presented in Figure 1. One can see that characteristic bends, positions of which are defined by the component ratio of the initial mixture, are present on all of the curves. The analysis of the results shows that at high and low AAc content, terpolymerization tends toward two extreme cases corresponding to the copolymerization of AAc-VEP and VA-VEP binary systems.

At low AAc content (curves 3, 4, and 5), minimums of rate values analogous to those described earlier² (at VA and VEP copolymerization) are observed. It is explained by a significant difference of comonomer reactivities. The summary terpolymerization rate grows, and minimums on the curves of its dependence on VEP relative content disappear as AAc concentration increases. The terpolymerization rate at VEP content increase diminishes in all investigated ranges of its concentration (curves 1 and 2). This is obviously caused by a prevalent influence of transfer and chain termination reaction with participation of peroxide.

The presence of parts of fast and slow rate change on the curves representing its dependence on VEP contents is explained by the fact that the process summary rate at low AAc content is determined by VEP homopropagation rate; at high AAc content, the rate is determined by transfer and chain termination with participation of VEP. These dependencies correspond to the results of VA-VEP² and AAc-VEP⁷ binary system copoly-

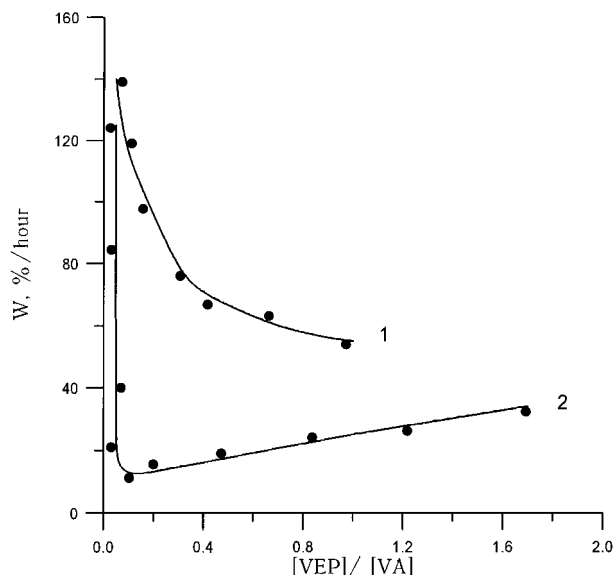


Figure 3 Dependence of VA, VEP, and AAc terpolymerization rate (W) versus $[VEP]/[VA]$ mole ratio at $[AAc]/([VA] + [VEP]) = (1) 0.33$ and $(2) 0.11$. (●) Experimental points; (343 K, methanol, $[AIBN] = 3 \times 10^{-2}$ kmol/m, $C_m = 4$ kmol/m³).

merization investigations. The fact that AAc content practically does not influence the terpolymerization rate at high VEP concentration confirms the above findings (Fig. 2). VEP binary copolymerization proceeding according to the rules of inhibited polymerization has been established earlier.^{3,7,8}

Figure 3 represents rates versus VEP concentration dependencies obtained by a calculation method, an equation of faint-inhibited terpolymerization being applied.⁹ Constant values used for the calculation of VA, VEP, and AAc terpolymerization rates at 333 K in methanol are indicated in Table I. It is obvious (Fig. 3) that the experimental values of the rates practically coincide with the dependencies calculated. This proves that the kinetics of synthesis of peroxide-containing terpolymers based on VA and VEP is

proceeding according to a faint-inhibited terpolymerization mechanism and confirms the experimental values of the constants.

At the same time, it is seen (Table II) that the theoretical composition calculated by the modifying composition equation¹⁰ using relative comonomer activities in a triple system (Table I) coincides satisfactorily with the experimental data. Thus, in a polymerizing system, VEP participates mainly in chain propagation reactions.

Kinetic features of terpolymerization with VEP have practical interest because VA and acrylic monomer polymerization is accompanied by the Trommsdorf effect, provoking formation of branched macromolecules and wide MWD of polymers. The method of regulating the Trommsdorf effect and its consequences by means of polymerization in the presence of a faint inhibitor and of a low-active monomer is known.¹¹ These last are unsaturated peroxide VEP and VA respectively in the systems examined. VEP introduction provokes the increase of chain transfer and termination reaction number with its (VEP) participation, which causes the formation of less active radicals that allow the regulation of the Trommsdorf effect intentionally. It is obvious (Fig. 4) that VEP introduction causes autoacceleration process displacement to higher conversion ranges and to its complete disappearance at a sufficiently high VEP content. Conversion at which autoacceleration is observed and the values of the last depend not only on VEP concentration and its exhaustion rate in this system but also on VA content; the high activity of its growing radical determines its effective participation in chain transfer reactions.

However, VA concentration influence on the Trommsdorf effect is considerably less than the influence of VEP concentration. The curves (Fig. 5) illustrating dependence of the content of nitrogen entering into terpolymer end groups at growing chain termination on DMF molecules show that this content grows with a mole ratio $[VA]/([AAc] + [VEP])$ increase. However, at high VEP

Table I Constants Characterizing Terpolymerization of VA (M_1), VEP (M_2), and AAc (M_3)

Copolymerization Constants						Constants Characterizing Chain Transfer to VEP		
r_{12}	r_{21}	r_{13}	r_{31}	r_{23}	r_{32}	C_{t_1}	$C_{t_2}^a$	$C_{t_3}^a$
0.075	13.32	0.10	2.00	1.40	0.19	1.810	0.0178	0.0624

^a C_{t_2} and C_{t_3} are shown in Ref. 7.

Table II Characteristics of Polyreactive Triple Oligoperoxides on the Basis of VA (M_1), VEP (M_2), and AAc (M_3)

No.	Composition of Monomer Mixture, Mole Fractions					Conversion (%)	Terpolymer Composition, Mole Fraction of Links					
	M_1	M_2	M_3	$\frac{M_2}{M_1 + M_3}$	$\frac{M_3}{M_1}$		Experimental			Calculated		
							m_{1i}	m_{2i}	m_{3i}	m_{1i}	m_{2i}	m_{3i}
1	0.8500	0.0500	0.1000	0.05	0.12	60.9	0.1449	0.4742	0.3809	0.1575	0.5000	0.3425
2	0.5000	0.2500	0.2500	0.33	0.5	48.0	0.0735	0.6940	0.2325	0.0554	0.6881	0.2565
3	0.2500	0.5000	0.2500	1.0	1.0	56.6	0.0996	0.8010	0.0994	0.0920	0.7950	0.1130
4	0.5000	0.5000	0.1000	1.0	0.25	62.0	0.1312	0.6960	0.1780	0.1400	0.6740	0.1860
5	0.5333	0.3334	0.1333	0.5	0.25	49.2	0.1791	0.5506	0.2703	0.2242	0.4955	0.2803
6	0.6400	0.2000	0.1600	0.25	0.25	38.8	0.1919	0.5115	0.2966	0.1864	0.4162	0.3974
7	0.3333	0.3334	0.3333	0.5	1.0	60.5	0.1430	0.7610	0.0960	0.1750	0.7150	0.1100
8	0.6000	0.3333	0.0667	0.5	0.11	48.6	0.0945	0.8555	0.0500	0.1100	0.8250	0.0650
9	0.4500	0.5000	0.0500	1.0	0.11	63.5	0.0818	0.5894	0.3288	0.1300	0.5660	0.3100

Copolymerization was carried in degassed and argon-filled calibrated ampules; 343K, methanol, $[AIBN] = 3 \times 10^{-2}$ kmol/m³.

concentration, its degree is less, because the share of chain transfer and termination reactions with VEP participation (as a more effective transfer agent) increases. The fact that the chain termination occurs principally by the growing radicals with VA end links conforms to an extraordinary high value of the constant that characterizes the efficiency of chain transfer by growing VA radical to VEP (Table I).

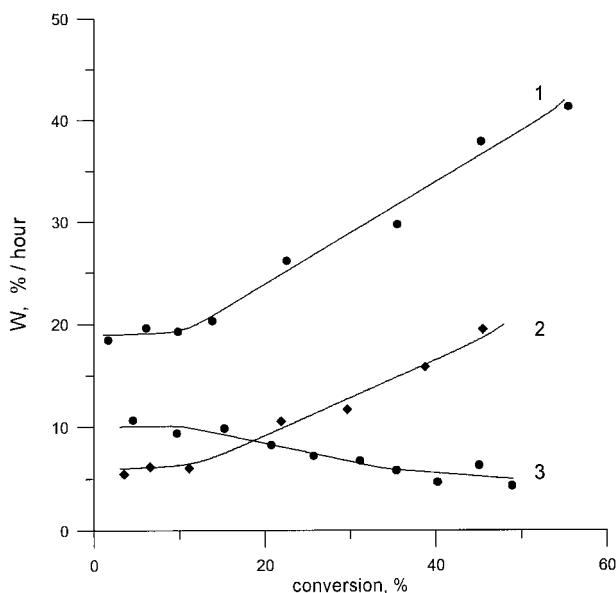


Figure 4 Dependence of VA, VEP, and AAc terpolymerization rate on conversion at mole ratio: $[VEP]/([VA] + [AAc]) = 0.02$ and $[AAc]/[VA] =$ (1) 0.25, (2) 0.11, and (3) $[VEP]/([VA] + [AAc]) = 0.11$ and $[AAc]/[VA] = 0.29$ (343 K, methanol, $[AIBN] = 1.5 \times 10^{-2}$ kmol/m³, $C_m = 4$ kmol/m³).

Terpolymer molecular-weight characteristic dependencies on VA and VEP concentration conform to the kinetic data (Fig. 6). Gel chromatograms prove the possibility that the system forms copolymers mainly of a unimodal or bimodal MWD character. At the same time, comparatively low values of oligomer polydispersity coefficients correspond both to MWD unimodal and bimodal character (Table III).

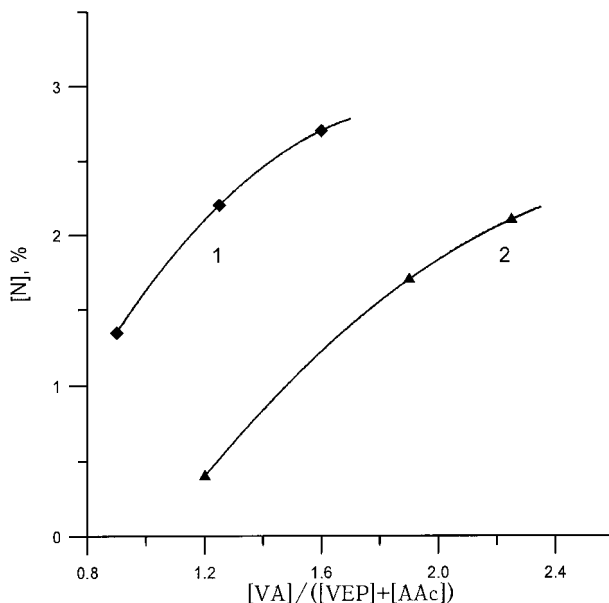


Figure 5 Dependence of nitrogen content (N) in VA-, VEP-, and AAc-based terpolymers obtained by copolymerization in DMF versus $[VA]/([VEP] + [AAc])$ mole ratio at VEP concentration: (1) 20 mol %, (2) 40 mol %; in monomer mixture (353 K, $[BP] = 2 \times 10^{-2}$ kmol/m³, $C_m = 4$ kmol/m³).

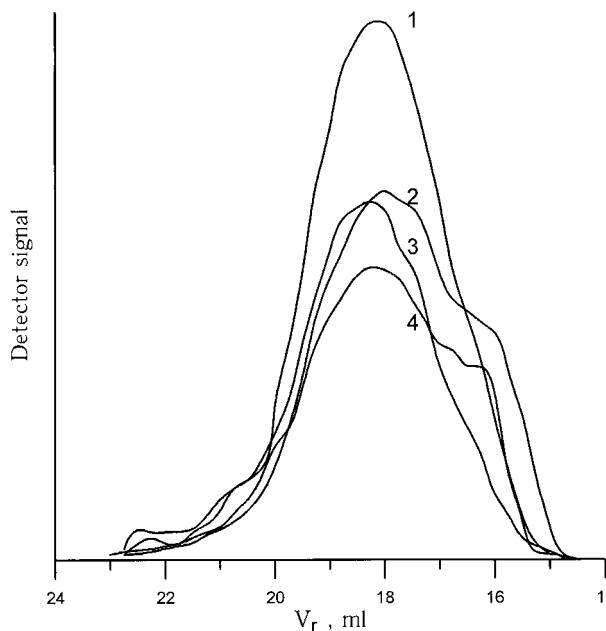


Figure 6 Gel chromatograms of terpolymers obtained at initial mole ratio: $[AAc]/[VA] = 0.11$ and $[VEP]/([VA] + [AAc]) = (1) 0.67$ and $(3) 0.25$; $[AAc]/[VA] = 0.25$ and $[VEP]/([VA] + [AAc]) = (2) 0.67$ and $(4) 0.25$; (353 K, DMF, $[BP] = 3 \times 10^{-2}$ kmol/m³) V_r is volume of eluent (tetrahydrofuran).

Such MWD character may be explained by the fact that the termination reaction at terpolymerization of the system studied proceeds by two mechanisms: biradical interaction termination and termination of low-active secondary radicals formed as a result of VEP transfer. This bimodality is obviously caused by the change in the ratio of different termination mechanisms as a result of the different ratios of the initial monomer mixture components and the different rates of their consumption.¹¹ The increase of VEP concentration in the system provides its presence at higher conver-

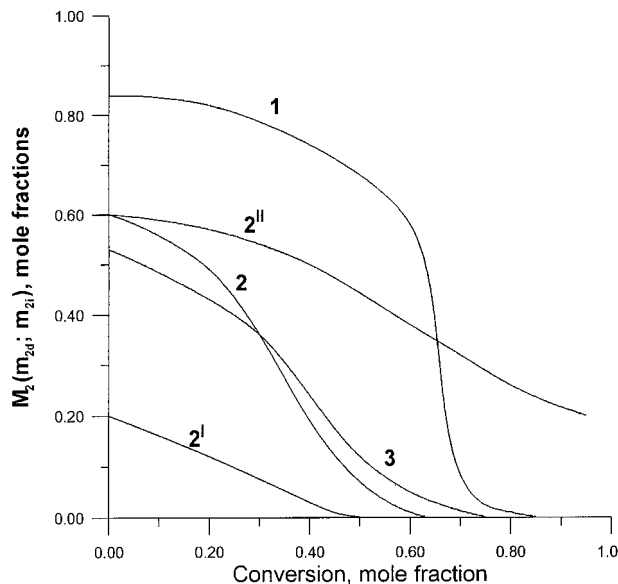


Figure 7 Dependence of VEP (M_2) concentration in ($2'$) monomer mixture and ($2''$) integral, and ($1-3$) differential contents of its links in terpolymers versus conversion at initial mole ratio: $[AAc]/[VA] = 0.25$ and $[VEP]/([AAc] + [VA]) = (1) 1.0$ and $(2, 2', \text{ and } 2'') 0.25$; $[AAc]/[VA] = 1.0$ and $[VEP]/([AAc] + [VA]) = (3) 0.25$.

sion (Fig. 7) and provokes the growth of transfer reaction fractions with the formation of low-active radicals. This results in the decrease of the molecular-weight values and of the oligoperoxide polydispersity coefficients. It is clear (Fig. 6) that the position of low-molecular fraction peaks caused by the chain termination reaction proceeding by this mechanism coincides in the gel chromatograms of all terpolymers. This fraction quantity (up to unimodal MWD) rises essentially during unsaturated peroxide concentration increase. The presence of a second peak displaced to a high-molecular-weight range is explained principally

Table III Characteristics of Terpolymer MWD Parameters on the Basis of VA, VEP, and AAc (Conversion, 70%)

No.	Component Mole Ratio		Parameters of MWD				
	$\frac{[AAc]}{[VA]}$	$\frac{[VEP]}{[AAc] + [VA]}$	M_N	M_W	M_Z	$\frac{M_W}{M_N}$	$\frac{M_Z}{M_W}$
1	0.11	0.67	750	1030	1410	1.35	1.37
2	0.11	0.25	650	950	1410	1.46	1.48
3	0.25	0.67	870	1300	1950	1.49	1.50
4	0.25	0.25	770	1180	1760	1.53	1.49

353K, DMF, $[BP] = 3 \times 10^{-2}$ kmol/m³.

by a biradical interaction termination, the fraction of which increases at VEP concentration decrease and at [AAc]/[VA] ratio increase, which results in faster exhaustion of peroxidic monomer (Fig. 7). This provokes growth of the mass share of a more high-molecular fraction and increases the tendency toward molecular-weight bimodal distribution.

CONCLUSIONS

Thus, theoretical and experimental analysis of some special features of the terpolymerization process and of peroxide-containing oligomer MWD proves that growing chain termination reactions proceed by two mechanisms: interaction of two radicals and termination of secondary radicals being formed as the result of the peroxide monomer chain transfer; the contribution of each one to the summary termination reaction is defined by the comonomer ratio and by the relative rate of their consumption in monomer mixture. The participation of a chain transfer agent VEP and of a low-active monomer VA in this reaction allows the control of the autoacceleration and the molecular-weight characteristics of peroxide-containing products. The practical value of investigated copolymerization features and new carbon-chain oligoperoxidic initiators consists in the possibility of the inten-

tional control of their colloidal-chemical initiating and modifying properties.

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