Control of Microstructure and Molecular Weight Distribution of Carbon-Chain Heterofunctional Oligoperoxidic Curing Agents

A. S. ZAICHENKO, S. A. VORONOV, A. I. KUZAYEV, O. M. SHEVCHUK, V. P. VASILYEV

State University "Lvivska Politechnica," S. Bandera 12, Lviv-13 290646, Ukraine

ABSTRACT: Polyreactive heterofunctional oligoperoxides (HFOPs) were synthesized by radical copolymerization of a peroxidic monomer (PM) with vinyl acetate and butyl acrylate. In this polymerizing system, PM participates mainly in chain propagation reaction. That allows us to use the known statistical terpolymerization composition equation for description of HFOP macrochain formation. At the same time, PM not only effectively terminates growing oligomer chains, but also reduces their total amount. Molecular weight characteristics of HFOPs were studied by gel permeation chromatography. It is proposed that their typical bimodal molecular weight distribution is a result of two competitive mechanisms: a biradical interaction termination and termination with secondary radicals formed as a result of PM transfer. The termination mechanism ratio depends both on composition and conversion level of the monomer mixture. The main regularities of a PM containing system polymerization determined by us allow us to control intentionally HFOP structural and molecular weight characteristics. The possibility of HFOP use for curing and modification of the castable mixtures on the basis of oligodieneurethanes and oligoacrylates has been shown. The use of such oligoperoxides provides improved basic physicochemical properties, an increase of thermoresistance, and fatigue resistance of composite rubbers. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2449–2455, 1998

Key words: peroxidic monomer; heterofunctional oligoperoxide; terpolymerization; molecular weight distribution; curing agent

INTRODUCTION

The presence of several radical-forming centers in the structure of carbon-chain oleosoluble oligoperoxides obtained by copolymerization of peroxidic monomer (PM) with other functional reactive monomers provides them with the ability to initiate polymerization and network-forming reactions.[1] It is obvious that network parameters that cause physicochemical and other exploitation properties of vulcanizates are determined by the nature and structure of curing agents. Conventional individual low-molecular curing agents— such as dicumyl peroxide, cyclohexanone peroxide, and benzoyl peroxide—possess precisely established structure and properties. There is unambiguity for multicenter oligomeric peroxides because of their composition, microstructure, and molecular weight distribution (MWD) heterogeneity.

The aim of this work is to investigate the possibility of structural and molecular weight characteristic regulation of heterofunctional oligoperoxides (HFOPs) based on vinyl acetate (VA), butyl acrylate (BA), and vinyl acetylenic ditertiary PM [2-*tert*-

Table I   Reactivity Ratio of Monomers in Terpolymerization

M_1	M_2	M_3	r_{12}	r_{21}	r_{13}	r_{31}	r_{23}	r_{32}
VA	VEP	BA	0.016	22.0	0.0398	4.952	0.3926	0.0366

butylperoxy-2-methyl-5-hexene-3-yne (VEP)] for obtaining the new surface-active curing agents with narrow, strictly definite structural distribution and MWD.

EXPERIMENTAL

VEP [CH_2=CH—C≡C—C(CH_3)$_2$—O : O—C(CH_3)$_3$] had the following characteristics after vacuum distillation: d_4^{20} = 0.867 (ref. 0.867); n_D^{20} = 1.4480 (ref. 1.4482); active oxygen content = 8.79% (Calcd. 8.75%). VA was purified by double column distillation at atmospheric pressure, and BA was purified under a vacuum. After that, their constants conformed to reference data.[2] Benzoyl peroxide was purified by recrystallization from ethanol. Dimethyl formamide (DMF) was dried and purified by the standard technique.[3]

Copolymerization was conducted in DMF medium in argon atmosphere at 353K. Conversion was monitored by dilatometric and gravimetric methods. HFOPs were purified by double precipitation from acetone solution to light petroleum and were dried under vacuum to constant weight. HFOP composition was determined by physical and physicochemical methods. The error of functional groups determination did not exceed 5 to 7%. MWD parameters were studied by a gel permeation chromatography method using a "Waters Co." gas-liquid chromatograph. Tetrahydrofuran was the eluent, its flow rate was 1.2 mL min^{-1}, and temperature was 298K. Column calibration technique and the calculation of M_N, M_W, and M_Z values and their ratios were described in previous work.[4]

RESULTS AND DISCUSSION

In an earlier investigation, the faint inhibitive ability of PM caused by its participation in chain transfer reactions to form radicals of lower activity than initial growing chains was described.[5] Some copolymerization kinetic features and properties of HFOPs formed with PM participation were also studied. However, until the present re-search, PM polymerization properties have not been used for purposeful regulation of macrostructure and microstructure, nor for HFOP MWD parameter control.

In addition, the high reactivity of growing radicals with VA chain ends in chain transfer[6] allows the examination of PM copolymerization mechanism under conditions that promote reaction with participation of PM peroxidic groups. It is necessary for the estimation of PM relative contributions into polymerization elementary stages (initiation, propagation, transfer, and termination) in which it can participate in consequence of the presence of two reactive centers in PM structure: double bond and peroxidic group.

To accomplish the intentional synthesis of a specific HFOP structure, a theoretical analysis of chain formation properties of VA, BA, and VEP copolymerization was performed.

VA-BA and VEP-BA copolymerization reactivity ratios were determined from the Alfrey–Price equation, with use of known values of Q and e parameters for VA, BA,[7] and VEP[8] (Table I). The values of the reactivity ratio for VA and VEP copolymerization in the triple system were determined from the polymerization results by a general sampling. The probabilities' product of monomers incorporation into chain has been considered. The analysis of macrochain formation at copolymerization was accomplished by numerical integration of the system of terpolymer composition modified equations.[9]

Theoretical dependencies of HFOP differential (or instantaneous) and integral composition on conversion are shown in Figures 1 and 2. It is evident that the difference of comonomer reactivity ratios causes their irregular consumption in the monomeric mixture and a significant composition heterogeneity of HFOPs that form at different conversion levels. The instantaneous content of monomer links in HFOP changes relative to the monomer concentration changes during conversion. The character of the monomer mixture composition alteration and the instantaneous and integral peroxide-containing co-oligomer compositions is determined by the initial ratio of the components. VEP and BA are foremost because

Figure 1 Dependence of VEP concentration (M_2) in monomer mixture (2^I), and of integral (2^{II}) and instantaneous (1, 2, 3) content of its links in HFOPs *vs.* conversion at initial mole ratio [VA]/[BA] = 0.33 and [VEP]/([BA] + [VA]) = 0.25 (1), 1.0 (2, 2′, 2″); [VA]/[BA] = 3.0 and [VEP]/([BA] + [VA]) = 1.0 (3).

they are the main competitors in the chain cross growth at triple system copolymerization. Exhaustion of the more active VEP and BA results in formation (at higher conversion level) of polymers that do not contain peroxide nor acrylate fragments. However, increasing BA concentration at a constant mole ratio [VEP]/([VA] + [BA]) in the initial mixture promotes more steady VEP consumption and formation of peroxide-containing oligomers at high conversion levels. Likewise, the increase of PM content influences BA consumption and the distribution of links of the latter in HFOP chain (Fig. 2). Such behavior in a copolymerizing triple system can be explained by the inclination of peroxidic and acrylic monomers to alternate due to the opposite polarization of their double bonds.

Average lengths of PM link blocks and the number and distribution of these blocks in a chain are the important characteristics of HFOPs as curing agents and modifiers. Calculated by the method of Zilberman,[10] parameters characterizing oligomeric chain structure are shown in Table II. It is clear that neither VA nor BA are inclined to form blocks of their own links. But, the more active VEP (especially at its high concentration or low BA content) forms blocks of different lengths. Moreover, the acrylate concentration increase not

only enhances the incorporation of low-active VA links into the chain, but it also causes the peroxide blocks' partition. This provides formation of HFOP, with a structure close to alternating at a definite monomer ratio. Satisfactory agreement of theoretical and experimental compositions of oligomers, obtained at different conversion levels, proves the correctness of theoretical dependencies. Moreover, it indicates that the chain formation process at copolymerization of a PM-containing system obeys well-known laws of statistical terpolymerization (Table III). On these grounds, one can conclude that VEP participates mainly in chain growth reactions in HFOP synthesis conditions (i.e., it performs the function of a monomer).

In addition, PM participation in chain transfer and termination reactions allows regulation of the length of HFOP synthesis kinetic parameters and individual oligomer chain length. This is very important for systems based on VA and acrylates, because the polymerization of these monomers is accompanied by the Trommsdorf effect, provoking formation of branched macromolecules and a wide MWD of polymers.[11] From Table IV and gel-chromatogram (Figs. 3 and 4) data, it can be seen that HFOPs show bimodal MWD as a general characteristic. This bimodal MWD at com-

Figure 2 Dependence of BA concentration (M_3) in monomer mixture (2^I), and of integral (2^{II}) and instantaneous (1, 2, 3) content of its links in HFOPs *vs.* conversion at initial mole ratio [VEP]/([BA] + [VA]) = 0.25 and [VA]/[BA] = 3.0 (1), 1.0 (2, 2′, 2″); [VEP]/([BA] + [VA]) = 1.0 and [VA]/[BA] = 1.0 (3).

Table II Dependence of Block Average Lengths (l) and Total Amount of Blocks Per 100 Copolymer Links (R) Vs. Monomer Mixture Composition and Level of Conversion

Conversion (mol fraction)	Instantaneous Composition of Monomer Mixture (mol fraction)			l (VA)	l (VEP)	l (BA)	R
	VA	VEP	BA				
0	0.2000	0.2000	0.6000	1.0	1.1	1.1	89.3
0.1	0.2215	0.1671	0.6114	1.0	1.1	1.1	89.4
0.2	0.2482	0.1278	0.6240	1.0	1.1	1.2	88.6
0.3	0.2820	0.0806	0.6374	1.0	1.1	1.3	85.9
0.4	0.3256	0.0274	0.6470	1.0	1.0	1.8	71.6
0	0.6000	0.2000	0.2000	1.0	1.4	1.0	83.2
0.1	0.6628	0.1606	0.1766	1.1	1.3	1.0	84.6
0.2	0.7398	0.1132	0.1470	1.1	1.3	1.1	86.1
0.3	0.8350	0.0567	0.1083	1.1	1.2	1.2	89.2
0.4	0.9410	0.0033	0.0557	1.6	1.0	1.2	76.8
0	0.3750	0.5000	0.1250	1.0	2.5	1.0	57.3
0.1	0.4147	0.4762	0.1091	1.0	2.6	1.0	55.4
0.2	0.4639	0.4453	0.0908	1.0	2.8	1.0	53.1
0.3	0.5261	0.4036	0.0703	1.0	3.0	1.0	50.2
0.4	0.6074	0.3452	0.0474	1.0	3.3	1.0	42.3

paratively low values of oligomer polydispersity coefficients may be the result of two termination mechanisms: biradical interaction termination and termination of secondary radicals of lower activity, formed as a result of PM transfer. This bimodality, then, is caused by a change in the ratio of the different termination mechanisms due to the change in the monomer mixture composition during the reaction process.

Thus, increasing the PM concentration in the monomeric mixture increases the number of transfer and termination reactions on the second-

ary radicals, resulting in a decrease of molecular weight values. It is clear from the increase of Vr values in the chromatogram (Fig. 3) and the decrease of HFOP polydispersity coefficients (Table IV). The presence of peaks corresponding to a low-molecular weight fraction on the MWD curves and their relative increase at rising PM content is an obvious indication of conducting the termination process according to this mechanism. Moreover, the position of low-molecular fraction peaks coincides in the gel chromatograms of all oligomers. The presence of a second peak dis-

Table III Characteristics of HFOPs on the Basis of VA (M_1), VEP (M_2), and BA (M_3)[a]

Monomer Mixture Composition (% mol)			Conversion (%)	Terpolymer Composition (% mol)					
				Experimental			Calculated		
M_1	M_2	M_3		m_1	m_2	m_3	m_1	m_2	m_3
29.6	26.0	44.0	78.7	8.5	30.1	61.3	7.8	37.2	55.0
20.0	20.0	60.0	85.0	5.3	23.9	70.8	7.3	25.0	67.7
12.5	50.0	37.5	93.8	2.3	52.6	45.1	3.6	54.9	41.5
22.7	9.1	68.2	84.3	9.6	15.4	74.9	9.7	11.4	87.8
81.8	9.1	9.1	60.8	62.2	12.2	25.6	69.7	15.2	15.2
37.5	50.0	12.5	47.8	2.7	60.3	36.9	2.6	73.2	24.5
45.0	50.0	5.0	50.4	3.4	72.9	23.7	4.8	83.9	11.3

[a] 353K, DMF, [BP] = $3.5 \cdot 10^{-2}$ kmol m^{-3}.

Table IV   Characteristics of HFOP MWD Parameters on the Basis of VA, VEP, and BA

| | Component Mole Ratio | | | MWD Parameters | | | | |
| | [BA] | [VEP] | | | | | $\dfrac{M_W}{M_N}$ | $\dfrac{M_Z}{M_W}$ |
Index	$\dfrac{[BA]}{[VA]}$	$\dfrac{[VEP]}{[BA] + [VA]}$	Conversion in 10 h (%)	M_N	M_W	M_Z		
1	3.00	0.10	77.3	1680	3340	6820	1.99	2.04
2	3.00	0.25	98.3	1260	1990	3660	1.59	1.84
3	3.00	1.00	81.4	1040	1500	2420	1.44	1.60
4	1.00	0.25	69.4	1220	1890	3460	1.55	1.83
5	1.00	1.00	83.1	870	1280	1940	1.48	1.52
6	0.33	0.25	66.5	940	1360	2280	1.45	1.67
7	0.33	1.00	65.2	950	1390	2220	1.46	1.60
8	0.11	0.10	75.6	1030	1750	2950	1.71	1.68
9	0.11	0.25	42.1	640	810	1070	1.27	1.31
10	0.11	1.00	56.6	880	1270	2010	1.45	1.58

placed to a high-molecular weight range (Fig. 3) can be explained principally by a biradical interaction termination, the fraction of which increases at decreasing PM concentration. The greater proportion of high-molecular weight fraction and the increased tendency toward bimodal distribution at a decreased VEP content in the initial mixture indicate that.

At high VEP and BA content in the reaction mixture, the regularity of their consumption re-

mains without changes to high conversion levels and the tendency to form HFOPs of unimodal MWD rises (Table IV), as described previously. It is obvious that both PM consumption and HFOP microstructure, as well as the character of dependence of molecular weight values and MWD *versus* unsaturated peroxide concentration, are determined by the [BA]/[VA] mole ratio. It is clear from Figs. 3 and 4 that low-molecular oligomers, with an increased tendency toward unimodal

Figure 3   MWD function of HFOPs obtained at initial mole ratio [BA] + [VA] = 3.0 and [VEP]/([VA] + [BA]) = 0.10 (1), 0.25 (2), 1.0 (3); [BA]/[VA] = 0.11 and [VEP]/([VA] + [BA]) = 0.10 (4), 1.0 (5).

Figure 4   MWD function of HFOP obtained at initial mole ratio [VEP]/([VA] + [BA]) = 1.0 and [BA] + [VA] = 0.33 (1), 3.0 (2); [VEP]/([VA] + [BA]) = 0.25 and [BA] + [VA] = 0.33 (3), 3.0 (4).

Table V   Constants Characterizing Chain Transfer in Copolymerization of VEP (M_2) at T = 333K

Monomer (M_1)	Styrene[a]	AAc[a]	MA[a]	VA	VA[b]
$\alpha \cdot Kt_1/Kp_1$	0.0289	0.0624	0.3090	1.810	2.676
$\alpha \cdot Kt_2/Kp_2$	0.0465	0.0370	0.0177	0.0078	0.0144

[a] Ref. 12.
[b] Experimental results at 343K.

MWD, are formed at high VA concentration. At low VEP concentration, VA influence on HFOP molecular weights and the character of MWD is more significant. The fact that chain termination principally occurs by reaction of the growing radicals containing VA chain ends with PM molecules conforms to high values for the constants that characterize the efficiency of transfer reaction by growing chains with VA ends (Table V). As a result, HFOP formation with a very narrow unimodal MWD is possible at high initial VA and VEP contents in monomer mixture (Fig. 5).

The use of these oligoperoxides as curing agents provides a route to the synthesis and modification of castable rubbers on the basis of oligodieneurethane elastomer (Table VI). Rubbers modified by oligoesteracrylate (OEA), with HFOP as curing agent, have higher breaking strength and thermoresistance at high fatigue strength retention, in comparison with those modified by only OEA.

Figure 5   Function of HFOP MWD (see index 9, Table IV) (○ = MWD of HFOPs obtained by basic alcolysis of initial product).

The optimum of the physicomechanical properties of the castable rubbers modified by OEA with HFOP is observed at the content of the latter ($\sim$ 0.5–0.7%). Analogously to the ideas about the reinforcement mechanism of high-molecular weight rubbers by OEA, the appearance of the microheterogeneous sites in the castable oligomeric rubbers can be presumed. In our opinion, the increase of the strength characteristics of castable rubbers at combined modification by OEA and surface-active oligomeric curing agent is caused by the orientation of HFOP on the phase boundary and its participation in network formation. The increase of rubber thermostability (Table VI) and sol-fraction content independence of the heating time at 423K confirm our suggestions about the formation of thermoresistant —C—C— bonds as a result of HFOP participation in the curing reaction.

It can be seen (Table VI) that the decrease of the strength parameters of the rubbers cured by dicumyl peroxide is prevented at HFOP use. We presume that it can be explained by the high plastizing ability of the latter.

CONCLUSIONS

The data obtained testify that the efficiency of a weak inhibitor VEP in the presence of a low-active monomer VA increases. This allows us to regulate the Trommsdorf effect of investigated system copolymerization and corresponds to literature data.[12] A narrow MWD of HFOP indicates termination of growing chains primarily by a transfer reaction to peroxidic groups of unsaturated peroxide and contradicts the explanation of the bimodal character of MWD curves by means of oligomer molecules branching at reinitiation by oligomer peroxidic groups. This allows intentional control of HFOP microstructure and MWD, and their use for modification and curing of castable composites.

Table VI   Characteristics of Castable Rubbers on the Basis of Oligodieneurethane Modified by HFOPs on the Basis of VA, VEP, and BA[a]

Obtaining Conditions and Rubber Properties	OEA	OEA + DCP[b]	OEA + HFO P
Vulcanization parameters (K/h)	353/3	353/3	353/3
Tension at 100% lengthening (MPa)	4.5/3.5	4.7/3.3	3.4/3.3
Breaking strength (MPa)	19.2/5.4	17.4/6.0	30.0/8.8
Relative lengthening (%)	750/500	810/660	780/560
Residual lengthening (%)	15/10	15/95	25/40
Sol-fraction content (%) (chloroform)	1.3	3.0	1.7
Resistance to crack formation (to 50 mm) at multiple bend of samples with zigzag ditch [cycles (10^3)]	400	165	300
Endurance at symmetrical variable bend with rotation (20% deformation) [cycles (10^3)]	10,000	2,500	10,000

Data were obtained in cooperation with L. Lanovskaya, Ph.D., Research Institute of Tyre Industry, Moscow.
[a] Numerator = value at 293K, denominator = value at 343K.
[b] DCP = dicumyl peroxide.

REFERENCES

1. S. A. Voronov, V. A. Puchin, V. S. Tokarev, Y. A. Lastukhin, E. M. Kiselyov, and A. S. Zaichenko, in *Catalytic and Initiative Systems for Polymerization and Modification of Polymers,* NPO Plastopolymer, Leningrad, 1984, p. 53.
2. Yu. S. Lipatov, A. E. Nesterov, T. M. Gritzenko, and R. A. Veselovskiy, *Handbook of Polymer Chemistry,* Naukova Dumka, Kiev, 1971.
3. A. Weissberger, E. Proskauer, J. A. Riddick, and E. E. Toops, *Organic Solvents,* Interscience Publishers, New York, 1955, p. 519.
4. A. I. Kuzaev, V. A. Linde, and Y. I. Estrin, *Vysokomol. Soyed.,* **A18,** 585 (1986).
5. V. S. Tokarev, S. S. Minko, A. S. Zaichenko, S. A. Voronov, R. V. Kucher, and O. Y. Ryabova, *Dokl. AN Ukr. SSR,* **292,** 1434 (1987).
6. S. N. Ushakov, *Polyvinyl Alcohol and Its Derivatives,* Vol. 1, Academii Nauk SSSR, Moscow, 1960.
7. G. E. Ham, *Copolymerization,* Chemistry, Moscow, 1971.
8. S. A. Voronov, V. A. Puchin, A. S. Zaichenko, and S. V. Shevchuk, *Ukr. Chem. Zhurnal,* **48,** 312 (1982).
9. S. A. Voronov, A. S. Zaichenko, V. A. Puchin, and V. S. Tokarev, *Dokl. AN Ukr. SSR,* **Ser. B,** 29 (1982).
10. E. N. Zilberman, *Vysokomol. Sojed.,* **B21,** 33 (1979).
11. V. L. Gladyshev and V. A. Popov, *Radical Polymerization at the Deep Conversion Level,* Nauka, Moscow, 1974.
12. S. A. Voronov, V. S. Tokarev, Y. A. Lastukhin, and V. A. Puchin, *Vysokomol. Sojed.,* **A22,** 1474 (1980).