Polyperoxide Surfactants for Interface Modification and Compatibilization of Polymer Colloidal Systems. I. Synthesis and Properties of Polyperoxide Surfactants

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ABSTRACT: Anhydride-containing polyperoxides were synthesized by copolymerization of $5-tert-$butylperoxy$-5-$methyl$-1-$hexen$-3-$yne with either maleic anhydride or its blends with styrene. The integral composition of the polyperoxides was theoretically calculated as the copolymerization process proceeded and its direct experimental evidence was obtained. In macrochain-formation behavior, the process was found to be consistent with the generally accepted regularities of binary and ternary copolymerization. By employing their polymerizational transformations, water-soluble polyperoxides exhibiting surface activity and initiating properties were obtained. In aqueous solutions, such polyperoxide surfactants form micellelike colloidal structures. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1217–1227, 2000

Key words: peroxide monomer; copolymerization; polyperoxide surfactant

INTRODUCTION

Peroxide polymers (PP) are specially designed reactive polymers with peroxide functionalities. Like other polymers with functional groups, PP may contain reactive —OO— groups which are end-functional macromolecules (**1.a**),[1,2] located in the backbone chain (**1.b**),[1–5] or connected with the main chain as substitutes (**1.c**),[1–6] as schematically illustrated in Scheme 1.

The problem of obtaining PP arose between the late 1950s and early 1960s in connection with the development of research on polymer modification, particularly by means of graft and block copolymer syntheses.[6] When PP are used as macroinitiators of radical polymerization, the first two types (Scheme 1, **1.a** and **1.b**) resulted in the formation of block copolymers,[6,7] while the third one yields graft copolymers,[6] which could be eas-

ily comprehended from their structure. Nearly at this same period, it was revealed that anionic living polymerization and polymerization with heterogeneous Ziegler–Natta catalysts can be applied for the production of various block copolymers.[8,9] Contrary to radical polymerization initiated with PP, the last two methods do not lead to the formation of homopolymers; therefore, the investigation of PP declined as a problem of interest. However, in the 1980s, we disclosed that PP of the type **1.c** are very effective modifiers for different polymer colloidal systems.[10] A new development of the research on this field is presented in this article.

It is known that PP containing reactive peroxide groups which are connected with the main chain as substitutes (structure **1.c**) can be obtained mainly in three ways, namely:

- By controlled oxidation of polymers[1,6];
- Polymer analogous transformation of polymers[6]; and
- Polymerization of peroxide monomers.[3,5–7,10]
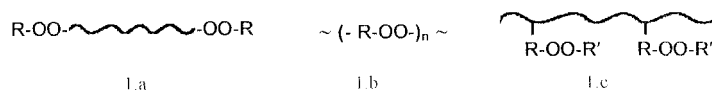
Scheme 1 Structure of peroxide polymers.

Provided that the peroxide groups of both the initial monomer and the polymer obtained are stable during PP synthesis, the last way is obviously the most prospective with a view to obtaining PP with preassigned structures and properties.

Today, about 200 peroxide monomers with different structures of both vinyl conjugated systems and peroxide groups[3,5] are known. Most of these peroxide monomers and polymers on their basis were synthesized at the Lviv Polytechnic State University.[5] One of the most promising peroxide monomers is that containing a sufficiently stable ditertiary peroxide group, $5-tert-$butylperoxy$-5-$methyl$-1-$hexen$-3-$yne (PM), which is obtained from the available technical products[11] (Scheme 2) with a high yield (>90%).

Many PP have been obtained through the copolymerization of this peroxide monomer with different vinyl and/or divinyl monomers[5,10] and some of them have been produced for industrial applications. Polyperoxides containing other reactive groups, for example, carboxylic[12] or pyridinic,[13] along with —OO— groups, are also of significant practical interest. We first synthesized such types of PP, naming them heterofunctional polyperoxides.[10] New spheres of application have been found for them, for instance, as self-curing film-forming materials,[14] adhesives for tire cords,[15] and polyreactive emulsifiers.[13,16] The most important properties of these types of PP are their capability to be localized and to interact at the interface of polymer colloidal systems, which facilitate the formation of compatibilizing interphase layers.[17] As a consequence, heterofunctional polyperoxides can be considered as a new type of polyreactive surfactants named polymer peroxide surfactants (PPS).

The synthesis of novel PPS, their notable properties, as well as the prospects for their practical applicability in creating polymer composites are considered in this series of articles. Precisely, in

this article, we elaborate on PPS containing peroxide and anhydride groups namely, copolymers of the peroxide monomer with maleic anhydride (PM–MA), and the ternary copolymer of the peroxide monomer with MA and styrene (PM–MA–S), whose structures are shown in Scheme 3. Much emphasis is laid on the features of their synthesis and their properties in aqueous solutions.

In this manner, the copolymers obtained via the copolymerization of the peroxide monomer PM with MA or their mixture with styrene (S) are of fundamental interest. This is relevant for many technological applications including activation of the surface of dispersed fillers, reinforced fibers of different natures, latex particles, and the interphase of polymer blends, owing to the structure of these PPS (Scheme 3) and their readiness to transform into peroxide polyelectrolytes in aqueous solutions (which results in the formation of the polymer acid PM–MAc and/or polymer salt PM–MS) (Scheme 4). Another significant and interesting feature worthy of note is their ability to react simultaneously or sequentially by radical and condensation polymerization mechanisms.

This work was performed with the aim to investigate the PPS synthesis behavior using the peroxide monomer PM and MA, as well as to study their colloidal and chemical properties, which are significant for their applicability in interface modification and compatibilization of polymeric colloidal systems.

EXPERIMENTAL

The peroxide monomer PM which was synthesized by the method described earlier[11] (Scheme 2) exhibited the following characteristics after vacuum distillation: $d_4^{20} = 0.867$ (ref. 11, 0.867), $n_D^{20} = 1.4480$ (ref. 11, 1.4482), and active oxygen
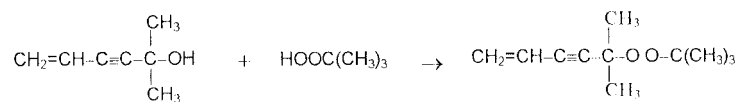
Scheme 2 Synthesis of $5-tert-$butylperoxy$-5-$methyl$-1-$hexen$-3-$yne.
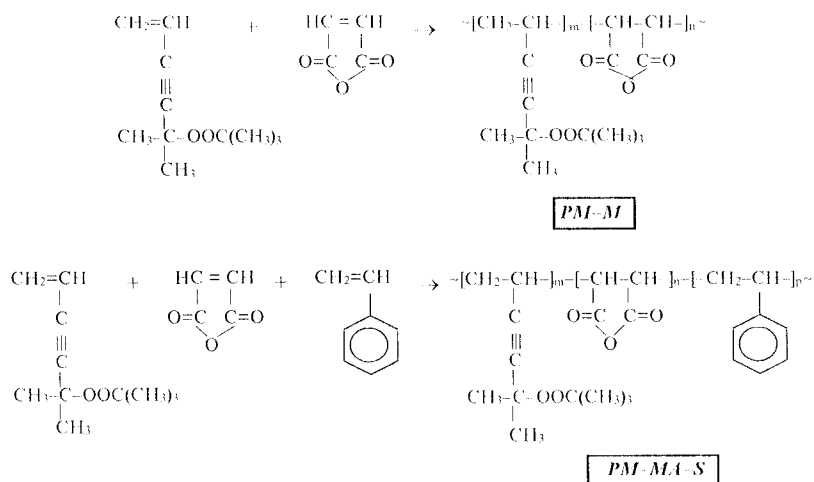
**Scheme 3** Synthesis of PPS containing peroxide and anhydride groups.

content of 8.7% (calcd 8.8%). The monomers used— MA and styrene—were conventionally purified before use and their characteristics agree well with the literature data.[18] Benzoyl peroxide (BP) was purified by recrystallization from ethanol and its active oxygen content was 6.5% (calcd 6.6%). *tert*-Dodecanethiol (DM), which was used as the chain-transfer agent, exhibited the following properties after purification: $d_4^{20} = 0.854$ (reference 0.854) and $n_D^{20} = 1.448$ (reference 1.448).

Copolymerization of PM with MA was performed in acetone at a temperature of 333 K under argon at an overall monomer concentration of 4 kmol/m^3 using BP at a concentration of 32 mol/m^3, while that of its mixture with styrene occurred through autoinitiation utilizing the PM peroxide groups under similar conditions. The conversion was evaluated using dilatometry and gravimetry. The resulting copolymers were purified by double precipitation from the acetone solution using a mixture of hexane and petroleum ether in a 1:1 wt ratio.

The intrinsic viscosity of the copolymers [η] was evaluated at 298 K in acetone using a Bishoff viscometer.[19] Copolymer molecular weights were determined using gel permeation chromatography (GPC) with a Waters Co. chromatograph using polystyrene standards. The eluent—tetrahydrofuran (THF)—was fed at a flow rate of 1.2 mL/min at 298 K.

The copolymer composition was determined by elemental analysis and potentiometric titration. During interactions between the anhydride-containing polyperoxides and water, the anhydride functions are opened to carboxylic groups (Scheme 4). Water-soluble salts of peroxide polymer acids are formed upon interaction with aqueous alkaline solutions (Scheme 4). Potentiometric titration was carried out in a thermostatic cell with an I-130 pH meter (Belarus) having stan-
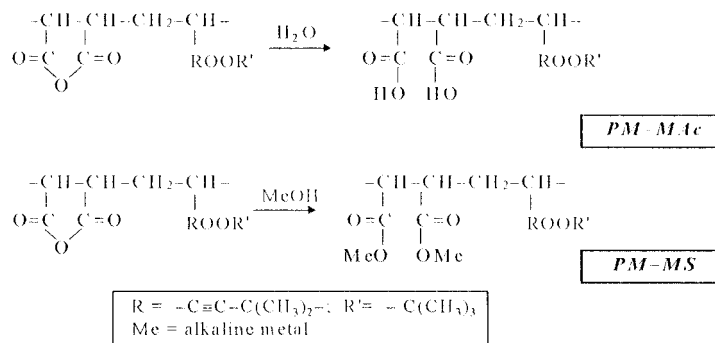
Scheme 4 Reactions of the anhydride groups of PM–MA.

Table I. Copolymerization of the Peroxide Monomer with MA

[PM] in the Monomer Mixture (mol %)	Conversion (%)	Polymerization Rate, $R \times 10^2$, (mol m^{-3} s^{-1})		[PM Units] in the Copolymer (mol %)		Intrinsic Viscosity $[\eta]$ (m^3 kg^{-1})	M_n
		Exp	Calcd	Exp	Calcd		
30	60.0	12.8	12.9	48.8	46.5	—	
50	54.5	10.0	10.0	56.6	66.6	13	7410
60	53.6	9.8	9.2	59.9	60.4	11	7240
70	45.4	7.8	7.8	68.7	65.5	10	7000
80	36.9	6.0	6.3	70.0	72.3	9	6800

dard glass and reference Ag/AgCl electrodes. The analysis procedure was as follows: The polymer sample was dissolved in an excess amount of a $0.1N$ KOH solution for the neutralization of the carboxylic group. A polymer salt solution in the concentration range 0.005–0.01 kmol/m^3 (in moles of monomer units considering the copolymer composition) was thus obtained and later titrated with $0.1N$ hydrogen chloride.

Surface-tension (σ) measurements were performed with a K12 KRUESS tensometer (Hamburg, Germany) by the Wilhelmy method with a platinum/iridium plate at 293 K, taking into consideration the time necessary to attain adsorption equilibrium. The critical micelle-formation concentrations (CMC) were evaluated from the surface tension of the PPS aqueous solutions. The turning point on the σ versus log c plot corresponds to the CMC value.

RESULTS AND DISCUSSION

Synthesis of the Polymer Peroxide

The data from the copolymerization of PM with MA (Scheme 3) are presented in Table I. It can be seen that the rate of the process, the composition, and the molecular mass of the anhydride-containing polyperoxides all depend on the composition of the monomer mixture.

On the basis of the data from Table I, the reactivity ratios (r) were estimated by Mayo and Lewis techniques as $r_{PM} = 0.36 \pm 0.12$ and $r_{MA} = 0.006 \pm 0.06$ using the copolymerization equation in the integral form.[20] With the aid of the values obtained, the composition diagram presented in Figure 1 was calculated in comparison with the experimental data indicated by squares on curve 1. As can be inferred from both Figure 1

and the reactivity ratios, PM is the more active comonomer. The high activity of PM is attributable to the presence of a highly conjugated multiple-bond system $>C{=}C{-}C{\equiv}C{-}$ in its structure, which is confirmed by the $Q = 1.83$ value.[21] The low value of r_{MA} shows that steric and electronic effects are obviously a handicap to the successive attachment of two MA units in the chain. This leads to the formation of alternating copolymers. A low value of the product $r_{PM} \times r_{MA} = 0.022$ indicates the susceptibility of the system to alternation.

From Figure 1, curve 2, and Table I, it can be seen that increasing PM concentration in the feed leads to a uniform drop in the rate of copolymer-
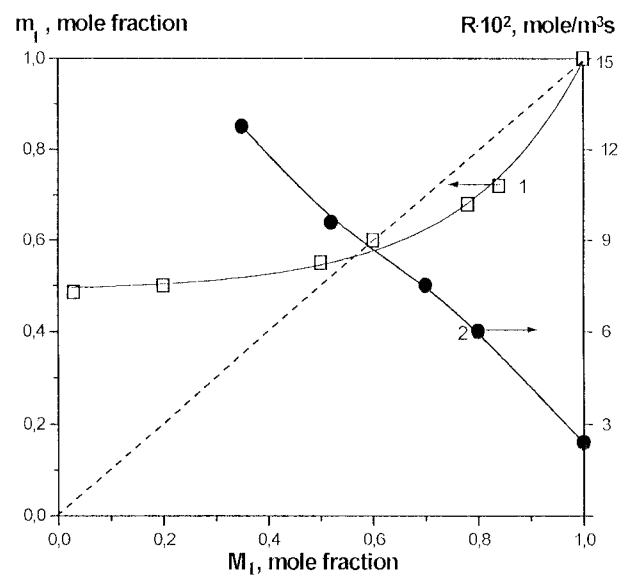
Figure 1 Effect of PM concentration, M_1, (1) on the PM–MA polyperoxide composition, m_1, and (2) on the rate of copolymerization, R. Solid lines were calculated; squares and circles are experimental data.

Table II. Constants Characterizing the Copolymerization of PM with MA at 333 K

$k_{d\text{PM}}$ 10^{-7} (s^{-1})	$k_{i\text{PM}}$ 10^{-7} (s^{-1})	r_{PM}	r_{MA}	$\alpha_{\text{PM}}c_{\text{trPM}}$	$\alpha_{\text{MA}}c_{\text{trMA}}$
0.73[a]	1.1	0.36 ± 0.12	0.006 ± 0.06	0.0177	0.309

[a] The value was evaluated using data from Table IV.

ization (R) and the polyperoxide molecular weight. This can be explained by the involvement of the peroxide group of PM in the chain-transfer and termination reactions, as was established in our previous work.[22] The theoretical rate curve was derived with the use of the rate equation for inhibited copolymerization proposed elsewhere[22] when the termination reactions occurs mainly due to the chain transfer to PM. For the copolymerization studied, this equation can be written as follows:

$$R = \frac{R_i(r_{\text{PM}} + 2F + r_{\text{MA}}F^2)}{\alpha_{\text{PM}}c_{\text{trPM}}r_{\text{PM}} + \alpha_{\text{MA}}c_{\text{trMA}}r_{\text{MA}}F} \quad (1)$$

where R_i is the rate of initiation; $F = [\text{MA}]/[\text{PM}]$, the MA-to-PM comonomer concentration ratio; and $\alpha_{\text{PM}}c_{\text{trPM}}$ and $\alpha_{\text{MA}}c_{\text{trMA}}$, the products of the constants determining the rates of the termination reaction of each type of polymer free-radical end-groups during chain transfer to PM.

To apply this equation, the values of R_i, $\alpha_{\text{PM}}c_{\text{trPM}}$ and $\alpha_{\text{MA}}c_{\text{trMA}}$ should be known. The last two products were both obtained from the experimental data presented in Table I with the aid of eq. (1) and their values are given in Table II.

The rate of initiation was derived from the following equation:

$$R_i = R_{i\text{PM}} + R_{i\text{PB}} = k_{i\text{PM}}[\text{PM}] + k_{i\text{PB}}[\text{PB}] \quad (2)$$

where $k_{i\text{PM}}$ and $k_{i\text{PB}}$ are the rate constants of initiation reactions caused by decomposition of O:O— groups of PM and BP, respectively. $k_{i\text{PM}}$ is given in Table II, while $k_{i\text{PB}}$ was calculated taking into consideration that $k_{i\text{PB}} = 2fk_{d\text{PB}}$, where $k_{d\text{PB}} = 2.1 \times 10^{-6}$ s^{-1} is the decomposition rate constant, and $f = 0.9$, the initiation efficiency.[23] It is evident that the theoretical values of R and the experimentally determined ones (both represented in Table I and Fig. 1) agree well at a PM concentration in the range from 30 to 100 mol %, when the prerequisite for preferential termination of the kinetic chain as a result of the chain-transfer reaction is met.

The differential and integral compositions of the resulting polyperoxide and the monomer mixture compositions were deduced as a function of conversion (Fig. 2, curves) by means of numerical integration of eqs. (3):

$$-\frac{dM_{\text{PM}}}{dS} = \frac{M_{\text{PM}}[M_{\text{PM}}r_{\text{PM}} + M_0(1 - S) - M_{\text{PM}}]}{\begin{array}{l} M_{\text{PM}}[M_{\text{PM}}r_{\text{PM}} + M_0(1 - S) - M_{\text{PM}}] \\ + [M_0(1 - S) - M_{\text{PM}}] \\ \times \{[M_0(1 - S) - M_{\text{PM}}]r_{\text{MA}} + M_{\text{PM}}\} \end{array}}$$
$$(3)$$

where M_{PM} is concentration of PM in mol/m^3; M_0, the initial overall monomer concentration in mol/m^3; and S, the monomer conversion in mol fractions.

In addition, the integral compositions of the copolymers during the copolymerization process were determined (Fig. 2, points). The polyperox-
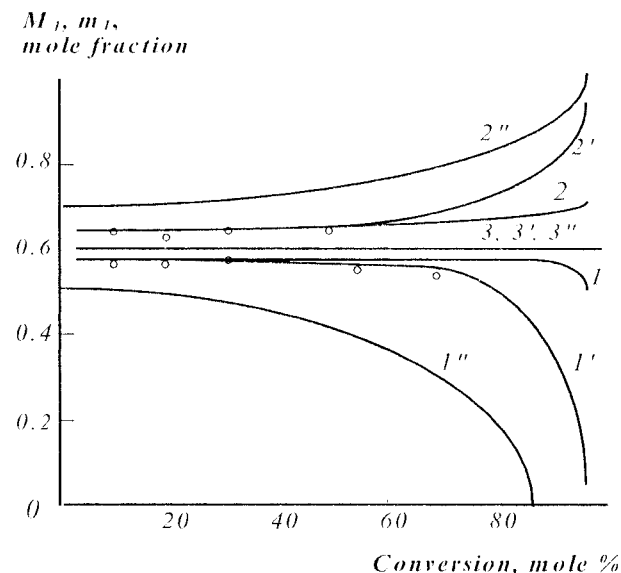
Figure 2 Influence of (1–3) the integral and (1′–3′) the differential composition of the copolymer as well as (1″–3″) the PM concentration on conversion during the copolymerization of PM with MA: (1,1′,1″) for $M_1 = 50$ mol %; (2,2′,2″), for $M_1 = 70$ mol %; (3,3′,3″) for $M_1 = 61$ mol %.

ide compositions obtained are consistent with the theoretically calculated values. These results constituted a strong argument that the reactivity ratios determined are authentic and that the formation of the PM/MA copolymer structure conforms to the common regularities of a statistical process. In general, the last statement is not certain because PM is consumed not only as a monomer, but also as an initiator and chain-transfer agent. However, the results obtained can be explained by the very low consumption of PM and the copolymers on the basis of secondary reactions such as initiation and chain transfer. Indeed, at a concentration of PM similar to 50 mol % and a temperature of 333 K, this consumption estimated from eq. (4)[24] using parameters from Table II gave a value of $n = 1.98$ %:

$$n = \frac{PM_s}{PM_0} = [1 - \exp(-k_d\tau)]$$

$$+ \frac{\alpha_{PM}c_{trPM}r_{PM} + \alpha_{MA}c_{trMA}r_{MA}F}{\alpha_{PM}r_{PM} + F} \quad (4)$$

where n is the fraction of PM consumed on secondary reactions in mol fractions; PM_s, the overall consumption of PM on the secondary reaction in mol/m^3; PM_0, the initial amount of PM in mol/m^3; k_d, the decomposition rate constant of —O:O— groups of PM, s^{-1}; and τ, the duration of copolymerization in seconds

It is apparent from the data in Figure 2 that for PM concentrations lower than the azeotropic composition (61 mol %) an enrichment of the copolymer in its units is observed at the initial stage of the process, yielding the exhaustion of PM at a 90% conversion (Fig. 2), while for PM concentrations higher than the azeotropic composition, the resulting polyperoxide is impoverished in its units, leading to the accumulation of PM in the monomer mixture. Due to the tendency of the PM–MA system to alternating copolymerization, varying the PM concentration from 50 to 70 mol % gives the formation of copolymers which are close in composition to the azeotropic composition. It can further be inferred from Figure 2 that the resulting PM–MA polyperoxide is not uniform in composition for all PM/MA ratios excluding those corresponding to the azeotropic composition.

Thus, in the copolymerization reaction with MA, PM acts mainly as monomer, confirming our previously obtained result that PM monomer consumption on the secondary reactions of initiation and chain transfer does not exceed ≈2–3%.[40] This allows one to obtain copolymers on its basis with the intended functionality as well as to study its copolymerization process by the well-known kinetic technique.

It should be pointed out that formation of PM–MA polyperoxides with a PM unit concentration < 50 mol % is hampered (Fig. 1). By introducing a third comonomer (e.g., styrene) into the system, the peroxide group content in the polyperoxides can be controlled. In addition, the initiation constant of the PM monomer at 333 K was found to be 7.2×10^{-8} s^{-1}, permitting one to perform autoinitiated copolymerization of PM with other monomers.

The results of the autoinitiated ternary copolymerization are shown in Table III. It is evident that introduction of styrene permits one to widely vary the peroxide group concentration in the copolymer, while application of a DM chain-transfer agent allows one to obtain polymer homologs of similar composition but different molecular weights. As in the case of binary copolymerization, PM is the most active monomer and the resulting terpolymers are rich in its units at all conversions. All the synthesized polyperoxides are well soluble in polar organic solvents like acetone and dioxane.

Thermal Decomposition of the Peroxide Monomer and Peroxide Polymer

Thermal decomposition of the peroxide groups of PM and PP occurs in accordance with Scheme 5. Gas chromatography revealed the formation of all the main low molecular weight products—acetone, *tert*-butyl alcohol, and toluene (the last is formed when the process occurs in benzene)— confirming the suggested scheme. It was also disclosed that decomposition of both PM and PP is accompanied by induced decomposition reactions caused by the attack of the free radicals present in the system on peroxide molecules, probably through a hydrogen-atom abstraction reaction (Scheme 6). In our opinion, it is the induced decomposition of PM that is responsible for its weak inhibiting behavior in the processes of radical copolymerization. This is because a low active secondary radical with a system of conjugated bonds is formed as a result of induced decomposition reactions. Addition of radical scavengers such as 2,6-di-*tert*-butyl-4-methyl phenol (Ionol) suppresses the induced decomposition of both monomeric and polymeric peroxides. For instance, the half-life of poly-PM in toluene at 423 K is increased in the presence of ionol from 56 to 92 s.

Table III.   Copolymerization of PM–S–MA

Composition of Initial Mixture (mol %)			[DM] (mol/L)	Conversion (mol %)	Copolymerization Rate, $R \times 10^2$ (mol m^{-3} s^{-1})		Copolymerization Composition (mol %)			$[\eta] \times 10^3$ (m^3 kg^{-1})
PM	S	MA			Exp	Calcd	PM	S	MA	
5	45	50	0	73.2	13.0	12.8	5.8	45.4	48.8	62.1
10	40	50	0	73.3	14.0	11.1	11.9	40.9	47.2	48.0
10	40	50	100	74.5	15.2	—	12.7	40.4	46.9	20.0
20	30	50	0	71.8	9.9	9.0	24.1	28.4	47.5	30.2
20	30	50	30	73.5	10.9	—	24.1	28.5	47.4	19.9
20	30	50	80	72.7	11.6	—	24.1	28.0	47.9	13.9
30	20	50	0	71.8	7.7	7.8	32.9	20.9	46.2	22.0
30	20	50	40	73.0	8.8	—	33.6	20.4	46.0	13.0
40	10	50	0	70.4	7.1	6.9	43.9	10.1	46.0	15.3
40	10	50	30	72.1	7.7	—	45.7	10.0	44.3	12.6
40	10	50	80	71.3	8.1	—	44.3	10.7	45.0	8.5
50	0	50	0	69.2	6.1	6.3	54.5	0	45.5	12.5
50	0	50	40	71.7	7.3	—	54.4	0	45.6	8.0
70	0	30	0	47.2	4.9	5.2	65.9	0	34.1	—

The half-lives of PM and its polymer are shown in Table IV in comparison with that of Luperox 130 (only monomolecular decomposition of peroxides was taken into consideration, neglecting induced decomposition). Having quite similar structures, these peroxides are characterized by close values of the decomposition rate. The half-life of both PM and its unit in polyperoxide at 333 K (the copolymerization temperature) exceeds 2×10^3 h, confirming the negligible consumption of peroxide groups during the synthesis of PPS.

Colloidal and Chemical Properties of PM–MA Polyperoxide Aqueous Solutions

Water-soluble salts of polyperoxy acids are formed during the interaction between the polyperoxide anhydride groups and alkalis (Scheme 4). The solubility of polyperoxides in water depends on both the hydrophilic-to-hydrophobic unit ratio in their macromolecules and the degree of carboxylic group neutralization by the alkali. The minimum concentration of maleinate
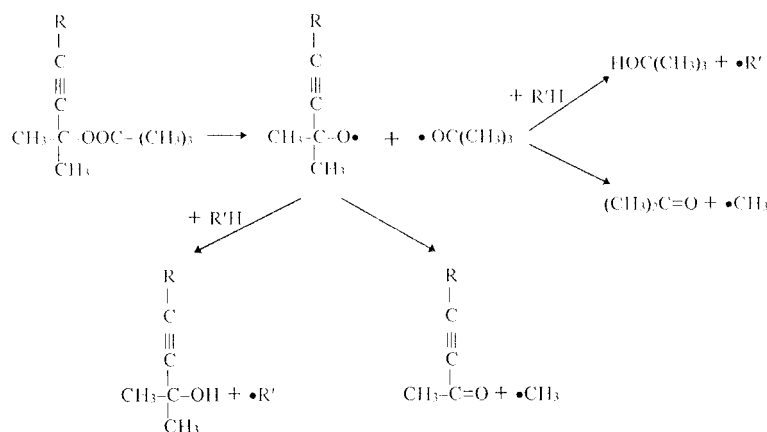
where R indicates CH$_2$=CH- for PM and
~CH$_2$-CH~ for PP

Scheme 5   Decomposition reactions of the peroxide groups in PM and PP.
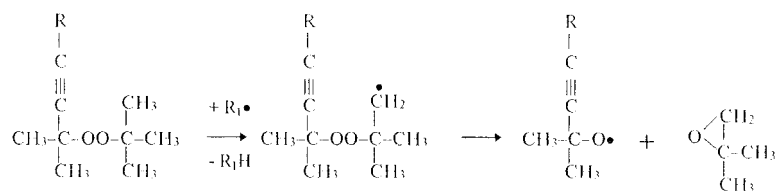
where R represents CH₂=CH- for PM
and ~CH₂-CH~ for PP

Scheme 6 Induced decomposition reactions of PM and PP.

units in the macromolecular chains required for PM–MA dissolution in water was found to be 28.7 mol % via turbidimetric titration. Transformation of this quantity to the molecular weight of the polymer confined in the aqueous solution by one ionic —COOK group yields a value of 287 molecular weight units. These results agree well with the literature data for this functional group.[25]

The presence of both hydrophilic and hydrophobic groups in MA-based polyperoxide molecules suggests their surface activity. This is evident from the σ versus log c plot, indicating a substantial decrease in the σ value of PPS solutions with increasing concentration (Fig. 3). In addition, some of these isotherms are characterized by turning points. We observed similar turning points for anion-active (on the basis of acrylic acid) and cation-active polyperoxides (on the basis
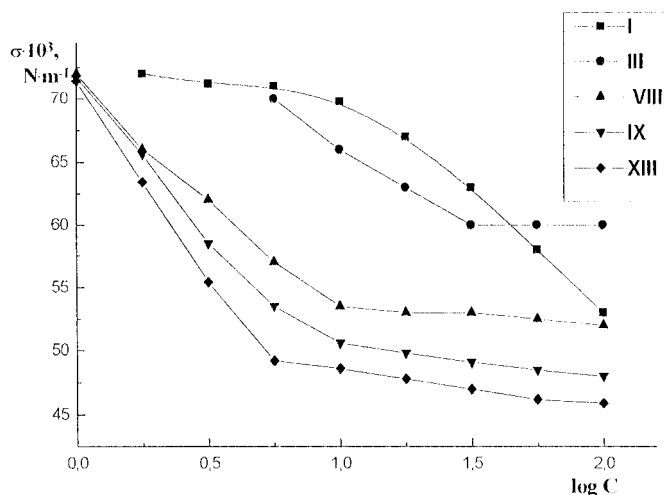
of 2−methyl−5−vinyl pyridine).[13] They are also typical for other polymer surfactants,[26,27] indicating the concentration at which the adsorption layer is saturated with surfactant macromolecules. In this manner, perhaps owing to the hydrophobic interactions between the alkylperoxy and phenyl substitutes, macromolecular aggregates are formed in the bulk solution, a process similar to the micelle formation of low-molecular weight semicolloidal surfactants.[28]

Consequently, the turning point on the surface-tension isotherms characterize polyperoxide aggregate formation, particularly the CMC value, which is thus obtained as a function of the copolymer composition and molecular weight (intrinsic viscosity) (Table V). The higher the concentration of hydrophobic alkylperoxy fragments in the binary copolymer, the lower the CMC

Table IV.   Half-life and Activation Energy of Peroxides

Peroxide		Half-life (min) at Temperature			Activation Energy (kJ/mol)
		413 K	423 K	433 K	
CH₂=CH—C≡C—C(CH₃)₂—OO—C(CH₃)₃	PM	172	50	27.5	143
CH₂—CH—C=C—C(CH₃)₂—OO—C(CH₃)₃	Poly-PM	233	82.5	30	151
(CH₃)₃C—OO—C(CH₃)₂—C≡C—C(CH₃)₂—OO—C(CH₃)₃	Luperox 130	192	68	24	154

Figure 3 Surface tension, σ, isotherm of water solutions of PPS. Legend designation in accordance with Table V.

value. In the case of ternary copolymers, replacement of styrene units by PM units also lowers the CMC and σ_{CMC} values. It is obvious that the alkylperoxy fragments hydrophobilize the macromolecule stronger than the phenyl rings.
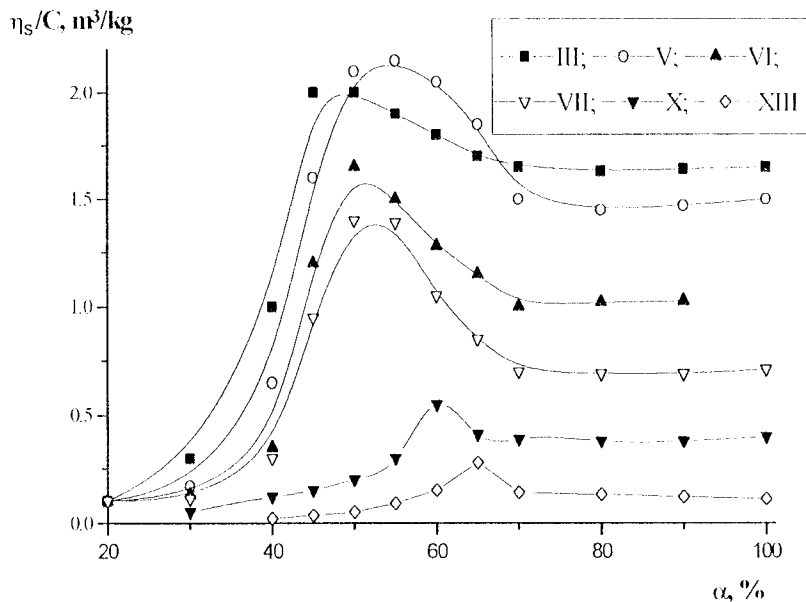
The degree of neutralization of the carboxylic groups (α) determines the PM–MA macromolecule conformation in the solution. As a result, an inflection characterizing the macromolecule conformational transition at their ionization process is observed in Figure 4, showing dependence of

the specific viscosity to a concentration ratio of a polyperoxide aqueous solution (η_s/C) on the neutralization degree of PPS (α). One can see that the trend in those dependencies is similar for all the polyperoxides irrespective of their having CMC values, indicating the change in conformation of separate macromolecules. Low η_s/C values at low degrees of polyperoxide ionization indicate the presence of compact globular macromolecular structures. For moderate degrees of ionization ($\alpha \geq 30$–55%), the PM–MA macromolecules exhibit

Table V.   Colloidal/Chemical Properties of the PPS

Copolymer Designation	Copolymer composition, mol %			$[\eta] \times 10^3$ $(m^3\ kg^{-1})$	CMC^a $(kg\ m^{-3})$	$\sigma_{CMC} \times 10^3$ $(N\ m^{-1})$
	PM	Styrene	MA			
I	5.8	45.3	48.9	62.1	none	—
II	11.9	40.9	47.2	48.0	none	—
III	12.0	39.9	48.1	20.0	35.5	53.2
IV	24.2	28.4	47.4	44.6	none	—
V	24.1	28.4	47.5	30.2	34.1	53.4
VI	24.1	28.5	47.4	19.9	20.5	52.3
VII	24.1	28.0	47.9	13.9	14.8	52.0
VIII	33.2	20.6	46.2	22.0	16.6	51.8
IX	34.2	20.0	45.8	13.0	10.5	50.0
X	43.9	10.1	46.0	15.3	9.9	50.0
XI	45.7	10.0	44.3	12.6	7.7	49.9
XII	44.3	10.7	45.0	8.5	5.0	49.5
XIII	54.5	0	45.5	13.0	5.0	48.8
XIV	54.4	0	45.6	8.0	4.0	48.6
XV	65.9	0	34.1	9.0	2.6	48.6

^{a} CMC values were determined at $\alpha = 100\%$.

η_s/C, m³/kg

Figure 4 Dependence of the relation of specific viscosity to concentration, η_s/C, of aqueous PM–MA solution on the degree of carboxylic group neutralization, α. Legend designation in accordance with Table V.

conformational transition, giving a more stretched structure experimentally indicated by a sharp increase in the η_s/C value. The following decrease of η_s/C is caused by some coiling behavior of the macromolecule under the influence of the solution ionic strength. Thus, the PM–MA macromolecules exist in aqueous solutions in the form of more or less packed globules, which are structural elements sorbed in the interfacial layers and capable of forming aggregates at definite concentrations.

Surface-active properties of PPS derived from the peroxide monomer and MA and the presence of reactive peroxide groups in their macromolecules make them prospective compounds for modification of the interface of different polymer colloidal systems, for instance, for the formation of interfacial compatibilizing polymer layers in water emulsions and dispersed-filled polyethylene, as will be shown in our next article.[29]

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