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A New Acrylamide-Based Peroxide Monomer: Synthesis and Copolymerization with Octyl Methacrylate

V. Samaryk,[†] I. Tarnavchyk,[†] A. Voronov,*[,‡] S. Varvarenko,[†] N. Nosova,[†] A. Kohut,[‡] and S. Voronov[†]

[†]*Department of Organic Chemistry, Lviv Polytechnic National University, 12 Bandera str., Lviv 79013, Ukraine, and* [‡]*Department of Coatings and Polymeric Materials, North Dakota State University, NDSU Dept. 2760, P.O. Box 6050, Fargo, North Dakota 58108-6050*

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ABSTRACT: *N*-[(*tert*-Butylperoxy)methyl]acrylamide (tBPMAAm), a new peroxide monomer containing a primary-tertiary peroxide group, was synthesized and employed for radical copolymerization with octyl methacrylate (OMA) to yield a novel functional polyperoxide (FPP). Copolymerization kinetics were analyzed to find tBPMAAm and OMA monomer reactivity ratios (r_1, r_2) and $Q - e$ values. Kinetic characteristics provide a way to control FPP composition and its reactivity in radical processes. It is expected that the developed functional polyperoxide containing long alkyl fragments provides an affinity to polymeric surface. At the same time, since the peroxide groups readily decompose at elevated temperatures, the FPP can be used as a macroinitiator of radical polymerization. As a result, we expect that in the future the FPP will be applied as an efficient modifier of the polymeric surface.

Introduction

Molecular composition of peroxide monomers (PMs) usually combines two active sites: double bonds and labile peroxide groups. Indeed, double bonds are capable of polymerization reactions and the labile peroxide group readily initiates radical processes[1−3] at elevated temperatures. Over 300 peroxides capable of polymerization have been synthesized to this point, including some which are manufactured industrially.[4,5] Common peroxide monomers are classified into three groups: (i) alkyl and aralkyl peresters of unsaturated mono- and dibasic acids; (ii) alkene−alkyne peroxides and hydroperoxides; and (iii) peroxide derivatives of styrene and α-methylstyrene.[3] The presence of the groups which are able to generate radicals and at the same time interact with the radicals determines the PM-specific behavior in polymerization reactions. The radical copolymerization of PMs has been widely studied.[1,6,7,11−13] Peroxide monomers can be copolymerized with vinyl and diene monomers without any additional radical initiators because of the peroxide group's decomposition.[1,6−13]

The new class of reactive polymers, called functional polyperoxides (FPPs), is based on the PMs. They have been recently designed and employed for synthesis and modification of polymer composites.[3] Along peroxide-containing fragments, there are hydroxyl, carboxyl, anhydride, or alkyl ($-C_6H_{13}$ to $-C_{15}H_{31}$) fragments that provide functional groups to the FPP structure. The ability of the functional groups to form chemical and/or physical bonds, combined with the homolytic decomposition of peroxide groups at elevated temperatures, makes FPP a unique experimental system for development of polymer composites, both *ex situ* and *in situ*.[3,13]

In fact, it has been shown that FPPs are multifunctional substances enabling the localization of reactive groups at the interface of in various colloidal systems such as emulsions (latexes) and polymer composites.[13−17] The FPPs readily undergo chemical reactions, resulting in the formation of polyperoxide initiator−emulsifiers (*inisurf*),[13,15,16] water-soluble macroinitiators,[13,16] and peroxide-modified fillers for polymer composites.[13,14,17,18]

Indeed, as it is deposited on organic and inorganic substrates, the FPPs interact with functional groups on the surface.[19] In this manner, the peroxide groups have been localized at the interface and further employed for chemical attachment of polyperoxides on planar and dispersed polymer surfaces.[13,20−23]

The immobilization of reactive peroxide groups at the surface allows for new ways for designing interface layers with predefined structures and natures, enabling special properties (biocompatibility, bactericidal properties, etc.) in the planar polymer surfaces,[24,25] developing new polymeric materials based on compatibilized polymeric blends,[26] and synthesizing "core-shell" polymer dispersions.[15,27,28]

In this study, we extend the PM library and develop a synthetic approach to a new acrylamide-based peroxide monomer, *N*-[(*tert*-butylperoxy)methyl]acrylamide (tBPMAAm).

This new peroxide monomer has been synthesized according to the reaction shown in Scheme 1.

We show that radical copolymerization of tBPMAAm with octyl methacrylate (OMA) results in the formation of a new functional polyperoxide we have called tBPMAAm−OMA (Scheme 2).

Indeed, tBPMAAm−OMA contains octyl methacrylate fragments which enable a primary interaction of the polyperoxide with a polymer substrate by van der Waals forces. In a specific case of polyolefins, the interaction between the octyl moieties of the polyperoxide and the polymer surfaces is especially important since polyolefins possess no functional groups that are able to facilitate either adsorption or covalent grafting. At the same time, the peroxide groups of the copolymer generate radicals or macroradicals through the decomposition of peroxide-containing fragments at elevated temperatures. We assume that the chain transfer reaction between the polyperoxide radicals and radicals

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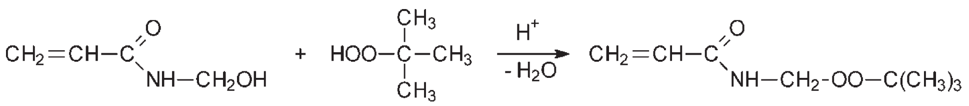
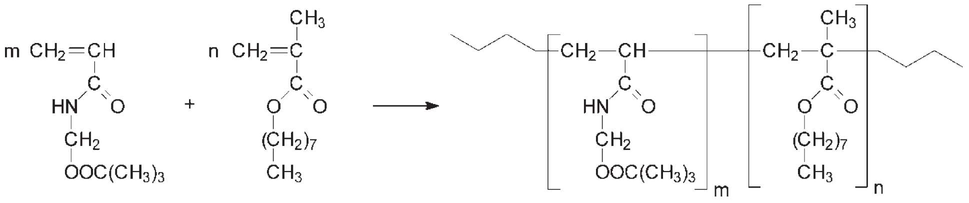
*Corresponding author. Telephone: +1 701 231-9563. Fax: +1 701 231-8439. E-mail: andriy.voronov@ndsu.edu.

Scheme 1. Synthesis of *N*-[(*tert*-Butylperoxy)methyl]acrylamide



Scheme 2. Copolymerization of *N*-[(*tert*-Butylperoxy)methyl]acrylamide with Octyl Methacrylate



at the polymer (e.g., polyolefin) surface, as well as recombination, results in a covalent attachment of the FPP layer to the substrate surface.[25,27]

Experimental Section

Materials. Acrylamide and *N*-(hydroxymethyl)acrylamide (HMAA) were purchased from TCI America and used as received. We dried the *tert*-butyl hydroperoxide (TBHP) (Alfa Aesar) over magnesium sulfate. Octyl methacrylate was synthesized via the peresterification of methyl methacrylate with 1-octanol according to techniques described elsewhere.[29] Azobisisobutyronitrile (AIBN) (Aldrich) was purified by recrystallization from methanol and cyclohexanone (Aldrich) was distilled before use.

Syntheses. *N-(tert-Butylperoxymethyl)acrylamide.* A solution of tert-butyl hydroperoxide (10.8 g, 0.12 mol) in diethyl ether (30 mL) was added dropwise to a solution of *N*-(hydroxymethyl)acrylamide (10.1 g, 0.1 mol) in diethyl ether (25 mL) at 5 −7 °C. The mixture was stirred and a solution of H_2SO_4 (2.94 g, 0.03 mol) in diethyl ether (20 mL) was added dropwise at 14−16 °C for 1 h. After stirring for an additional 3 h at 22−25 °C, the organic phase was separated, washed in series with water, 5% aq Na_2CO_3, and water until pH 7, dried over $MgSO_4$ for 12 h, and evaporated under reduced pressure to afford *N*-(*tert*-butylperoxymethyl)acrylamide at 98% purity as a colorless transparent liquid (15.5 g, yield 82%), $d_4^{20} = 1.010$, $n_D^{20} = 1.458$. MR_D: calcd, 45.91; found, 46.15. FT-IR (film): 3400−3200 cm^{-1} (N−H), 1670 (C=O, amide I), 1630 (C=C), 1540 (N−H, amide II), 880 (O−O). ^1H NMR ($CDCl_3$, 500 MHz): δ 1.26 (s, $(CH_3)_3C$, 9H); 5.17 (d, CH_2OOt-Bu, $J = 6.53$ Hz, 2H); 5.74 (dd, CH_2=C, $J = 10.36$, 1.21 Hz, 1H); 6.15 (dd, C=C*H*, $J = 17.03$, 10.36 Hz, 1H); 6.37 (dd, CH_2=C, $J = 17.03$, 1.22 Hz, 1H); 6.57 (s, NH, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, solvent peak as reference): δ 26.27 ($(CH_3)_3C$); 73.55 (CH_2OOt-Bu); 80.75 ($C(CH_3)_3$); 127.69 (CH_2=C); 130.53 (*C*=CH); 165.72 (*C*=O). Anal. Calcd for $C_8H_{15}NO_3$: C, 55.47;, H, 8.73; N, 8.09; $[O]_{act}$, 9.24. Found: C, 55.40; H, 8.83; N, 8.21; $[O]_{act}$, 9.52 (by chromatography of decomposition products). Molecular weight: calcd for $C_8H_{15}NO_3$, 173.21; found, 168 (by cryoscopy in benzene).

Copolymerization of tBPMAAm and OMA. N-(*tert*-Butylperoxymethyl)acrylamide, octyl methacrylate, and AIBN (0.004−0.025 M) were dissolved in cyclohexanone. The total concentration of monomers was 2 M. The reaction mixture was purged with argon at room temperature for 30 min. The polymerization was carried out under an argon blanket at 60−70 °C for 2−3 h until the monomer conversion of 25−45%. Samples of the reaction mixture (1−1.5 mL) to be tested chromatographically were taken periodically. The progress of the reaction was monitored by an analysis of the samples for monomer content using liquid chromatography. The copolymer was isolated by precipitation in methanol and purified by multiple reprecipitation in methanol from an acetone solution. Finally, the purified polymer was dried under reduced pressure at room temperature until a constant weight was obtained. The copolymer, which contained less than 55 mol % peroxide monomer, was well soluble in acetone and nonsoluble in methanol. The molecular weight of the copolymers has been determined by gel permeation chromatography (M_w = 154 000−181 000 g/mol, PDI = 1.98−2.15).

Characterization. Fourier transform infrared spectra were taken with a Varian Excalibur FTS 3100 spectrometer with a resolution of 4 cm^{-1}.

^1H NMR spectra were recorded at 500 MHz on a Varian VXR-500 NMR spectrometer.

Determination of the concentration of each monomer during copolymerization was performed on the liquid chromatograph "Laboratorni Pristroje" (Prague) using a differential refractometer (RIDK-102). The components of the polymerizate were separated on column CGC-C18 ($d = 3$ mm, $l = 300$ mm, NTP = 5000) with methanol as an eluent. Each monomer concentration was determined by the internal standard method.

Copolymer composition has been determined from tBPMAAm−OMA thermolysis data using gas chromatography. The data was compared to the calculated copolymer composition.

Monomer reactivity ratios of tBPMAAm and OMA in copolymerization were determined using approaches first developed by Feinmann-Ross[30] and Skeist.[31]

Thermogravimetric analysis (copolymer thermolysis) and differential scanning calorimetry were carried out simultaneously on the same portion of the sample during a single temperature program using a Paulik−Paulik−Erdey OD-102 derivatograph. The specimen was placed in an uncovered ceramic holder and heated at a rate of 0.6 °C/min to 200 °C in the atmosphere of released volatiles and argon.

Geometry optimization of the polyperoxide molecule was performed using the molecular mechanics MM+ module and PM3 semiempirical calculation methods in the HyperChem 6.03 molecular modeling program package. Using Fletcher−Reeves and Polak−Ribiere algorithms of semiempirical optimization followed by molecular mechanics optimization with the steepest descent algorithm, energy minimization was performed.

Results and Discussion

Synthesis and Characterization of tBPMAAm. The proposed approach to the synthesis of the peroxide monomer tBPMAAm is based on the interaction of *N*-(hydroxymethyl)acrylamide with *tert*-butyl hydroperoxide (Scheme 1). Among various solvents, diethyl ether has been found out to be the most suitable reaction medium for high-yield synthesis of the desired peroxide monomer. The yield depends considerably on the initial concentration of the reactants and the ratio of the catalyst (H_2SO_4) to HMAA. The HMAA concentration of 0.13−0.18 g/mL and the molar ratio of reactants (HMAA:TBHP:H_2SO_4 = 1:1.2:0.3), as described in the

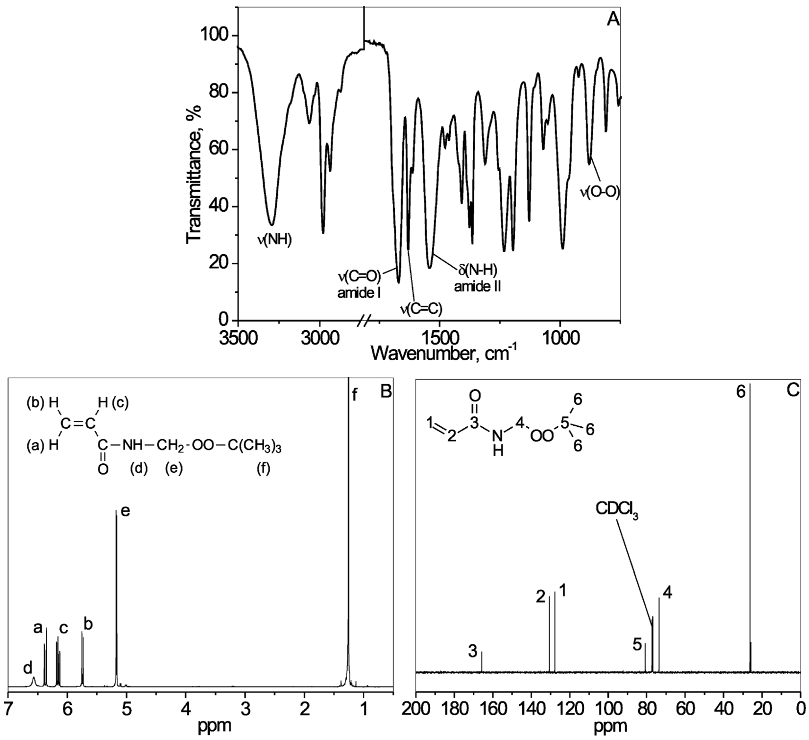


Figure 1. FTIR (A), ^{1}H NMR (B), and ^{13}C NMR (C) spectra of peroxide monomer tBPMAAm.

Experimental Section of this paper, result in the highest monomer yield (80−82%). When we increase the excess of TBHP in the reaction, it does not enhance the monomer yield, whereas when a greater amount of the catalyst is used, the reaction selectivity has been reduced. When we decrease the concentration of the catalyst, it leads to a lower conversion and the appropriate yield of the desired peroxide monomer.

The chemical structure of the synthesized monomer was confirmed by FTIR,^{1}H NMR and ^{13}C NMR spectroscopy (Figure 1) and the good agreement of found and calculated molecular refraction values (46.15 and 45.91, respectively).

Radical Copolymerization of tBPMAAm with Octyl Methacrylate. To evaluate the reactivity of the new PM in radical copolymerization, kinetic characteristics for copolymerization of tBPMAAm with OMA have been studied. The reaction order with respect to the initiator was studied in radical copolymerization at 60 °C, an initial monomer concentration of 2 M ([tBPMAAm$_0$] = 0.6 M, [OMA$_0$] = 1.4 M), and varying initiator AIBN concentrations (0.004 − 0.025 M). The kinetic curves and logarithmic plot of the monomers' consumption at different AIBN concentrations are presented in Figure 2. The reaction was carried out to the 32−43% total conversion, resulting in a monomer conversion of 13−16% for tBPMAAm and 35−55% for OMA. The reaction order in initiator was determined by the tangent of the slope angle (plot 6 in Figure 2). The obtained value, 0.72 ± 0.02, supports neither the suggestion that bimolecular termination of the growing macroradicals occurs (in this case, the reaction order should be 0.5) nor that termination by chain transfer reactions occurs, resulting in low-active radicals formation (when the reaction order is 1.0). Apparently, there is a mixed termination at copolymerization of peroxide monomer tBPMAAm when the growing chains undergo both bimolecular and linear termination.

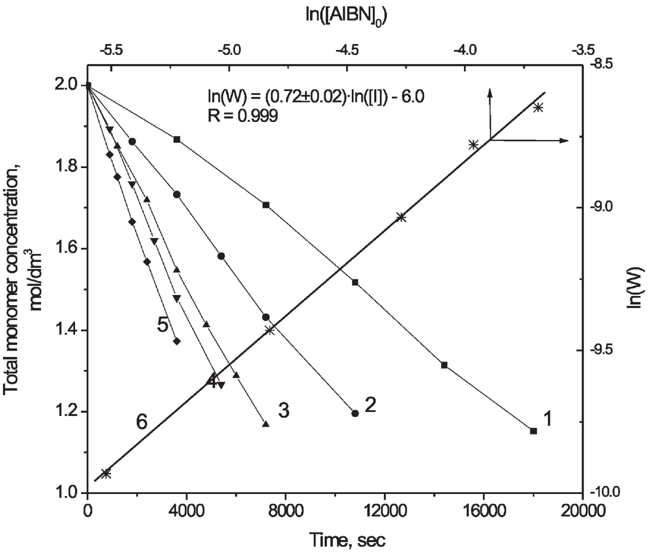


Figure 2. Kinetic curves of the comonomers' consumption in copolymerization of tBPMAAm with OMA at various initial concentrations of AIBN (1, 0.004 M; 2, 0.008 M; 3, 0.014 M; 4, 0.019 M; 5, 0.025 M). The logarithmic plot for the initial rate of the monomers' consumption vs the AIBN concentration is also shown (curve 6).

A satisfactory linearization for the curve $W_0 - [\mathrm{AIBN}]_0^{0.72}$ ($R = 0.998$) (Figure 3) confirms the experimental determination of the reaction order in the initiator. As shown in Figure 3, the straight line approximation equation contains the statistically determined free term (3.2 ± 0.8) × 10^{-6} mol/L·s^{-1}):

$$W_0 = (0.0025 \pm 0.0002)[\mathrm{AIBN}]^{0.72} + (3.2 \pm 0.8) \times 10^{-6}$$

This free term in the approximation equation corresponds to the degree of self-initiation in copolymerization. The result shows that although AIBN initiation dominates in the investigated concentration range, additional initiation of the copolymerization proceeds due to thermolysis of the peroxide groups in the tBPMAAm fragment. A low degree of self-initiation during copolymerization was observed (not exceeding 3−4%).

In order to determine the instantaneous copolymer composition as a function of conversion for the given comonomer feed, one can use the integrated form of the Mayo−Lewis copolymerization equation.[31] The most useful method is one developed by Skeist,[32] in an equation following the drift in composition of both the feed and the copolymer formed.

Writing a material balance for the monomer, one can determine the copolymer's overall composition for any conversion simply from an examination of the amounts of initial and residual monomer. After the integration, the equation transforms in the useful form, relating the degree of conversion to the change in the feed composition. We employed an integrated form of the Skeist equation to determine monomer reactivity ratios for OMA (r_2) and tBPMAAm (r_1) based on experimental monomer conversion values (determined by liquid chromatography):

$$1-\frac{\mathrm{M}}{M_0}=1-\left(\frac{f_1}{f_{10}}\right)^{\alpha}\left(\frac{f_2}{f_{20}}\right)^{\beta}\left(\frac{f_{10}-\boldsymbol{\delta}}{f_1-\boldsymbol{\delta}}\right)^{\gamma}$$

where f_1 is the tBPMAAm mole fraction in monomer mixture, f_2 is the OMA mole fraction in monomer mixture, and $f_2 = 1 - f_1$;

$$\alpha=\frac{r_2}{1-r_2}\quad \beta=\frac{r_1}{1-r_1}\quad \gamma=\frac{1-r_1r_2}{(1-r_1)(1-r_2)}$$

$$\boldsymbol{\delta}=\frac{1-r_2}{(1-r_1)(2-r_1-r_2)}$$

The calculations give the monomer reactivity as follows: $r_1 = 0.25$ and $r_2 = 4.2$ (shown in Table 1). Similar data ($r_1 = 0.18$ and $r_2 = 3.8$) have been yielded using Feinmann and Ross's approach[30,31] (a differential form of the Mayo−Lewis copolymerization equation). Data coincidence indicates that radical copolymerization of tBPMAAm with OMA can be described by classical kinetic peculiarities, both at the initial polymerization stage (low conversion degree) and at higher conversion levels.

Figure 4 shows the variation in the copolymer composition as a function of the comonomer feed composition both for the experimental and calculated monomer reactivity ratios[30,31] based on the Mayo−Lewis equation.

$$F_1=\frac{r_1f_1+f_2}{r_1f_1+2f_2}$$

where F_1 = tBPMAAm mole fraction in polymer.

The presented plots are in very good agreement, proving that copolymerization of tBPMAAm with OMA can be described by a classical copolymerization equation (the Mayo−Lewis equation). Moreover, the data obtained can be applied for the syntheses of functional polyperoxides that have different controllable amounts of peroxide-containing tBPMAAm fragments.

On the basis of ref 33, *Q* and *e* values were assigned to the new peroxide monomer. The obtained data is shown in Table 1. To this end, the effect of total conversion on the instantaneous tBPMAAm fraction (F_1) and the average tBPMAAm fraction (F_{1av}) in the copolymer has been estimated. Figure 5 shows the change in the peroxide monomer content in the feed monomer mixture (f_1) and the resulting copolymer (F_1) with a total conversion (when $(f_1)_0 = 0.5$).

Increased conversion results in a growth in the average peroxide monomer fraction (F_{1av}) in the copolymer (Figure 5). It can be seen that the OMA monomer is consumed faster, and by increasing the conversion, the monomer mixture becomes enriched with tBPMAAm. For the copolymerization, when $(f_1)_0 = 0.5$ (shown in Figure 5), the tBPMAAm fraction in the monomer mixture is about 90% at total conversion (0.7). Thus, the average peroxide monomer fraction in copolymer F_{1av} changes by about 12%. Therefore, it can be concluded that to synthesize the copolymer with a variation of average peroxide monomer fractions not exceeding 5% ($F_{1av} - (F_{1av})_0 \leq 0.05$, when $(f_1)_0 = 0.5$), the reaction should be carried out to the 40% conversion.

Interestingly, *Q* and *e* values for tBPMMA (0.17 and 0.13) reveal considerable changes in activity when compared to acrylamide (AAm) ($Q = 1.18$, $e = 1.3$). Both *Q* and *e* values

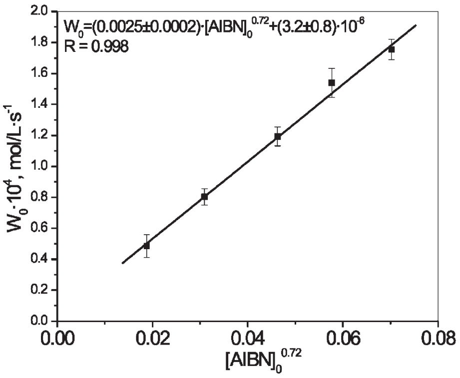


Figure 3. Determination of copolymerization self-initiation by the tBPMAAm peroxide monomer.

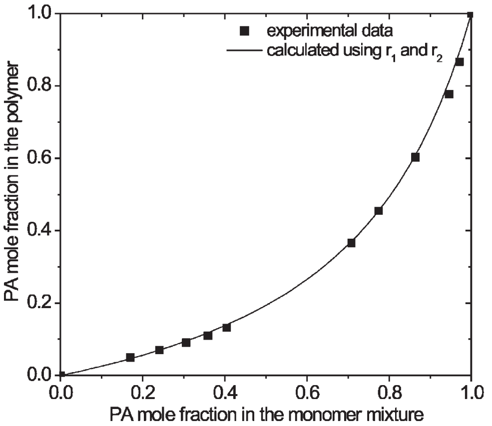


Figure 4. Calculated and experimental tBPMAAm content in copolymer composition vs tBPMAAm content in the initial feed mixture.

Table 1. Monomer Reactivity Ratios and *Q*−*e* Values for Copolymerization of tBPMAAm and OMA

	monomer reactivity ratios (Skeist equation)		monomer reactivity ratios (Feinmann−Ross equation)		*Q*−*e* parameters	
comonomer	r_1	r_2	r_1	r_2	*Q*	*e*
tBPMAAm (1)	0.25 ± 0.1		0.18 ± 0.1		0.17	0.13
OMA (2)		4.2 ± 0.5		3.8 ± 0.5	0.78	−0.31

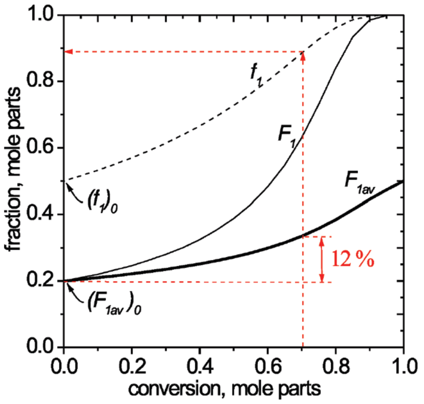
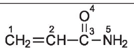
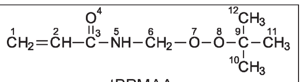


Figure 5. Change in the peroxide monomer content in the feed mixture and the copolymer brought about by changing the total conversion (f_1, instantaneous peroxide monomer content in the feed mixture; F_1, instantaneous peroxide monomer content in the copolymer; F_{1av}, average peroxide monomer content in the copolymer; $(f_1)_0$, initial peroxide monomer content in the feed mixture; and $(F_{1av})_0$, average initial peroxide monomer content in the copolymer).

Table 2. HyperChem Data for tBPMAAm and AAm

Monomer / Parameter	 $\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}(=\overset{4}{O})-\overset{5}{N}H_2$ AAm	 $\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}(=\overset{4}{O})-\overset{5}{N}H-\overset{6}{C}H_2-\overset{7}{O}-\overset{8}{O}-\overset{9}{C}(\overset{12}{C}H_3)(\overset{10}{C}H_3)-\overset{11}{C}H_3$ tBPMAAm
Torsion angle (φ°) $C^1=C^2-C^3=O^4$	179.9° ÷ 180°	17.6° ÷ 22.8°
Dipole moment of molecule, μ_x	3.81	3.32 ÷ 3.22
Projection of dipole moment μ_x on C=C bond	3.77	-0.33 ÷ -0.26
Angle between molecule dipole and C=C bond	8° ÷ 9°	84° ÷ 85°

are decreased for tBPMAAm because it has a (tert-butylperoxy) methyl substituent at the nitrogen atom. To explain the differences in the *Q* and *e* values between AAm and tBPMAAm, we performed analyses of the molecular configurations of tBPMAAm and AAm using the HyperChem molecular modeling package. Torsion angles of $C^1{=}C^2{-}C^3{=}O^4$ fragments, molecule dipole moment, dipole moment projection to the double bond and angles between C=C bond vector and the molecule dipole moment have been evaluated using HyperChem (Table 2). To show changes in the torsion angle ($\varphi°$), the planes formed by $C^1{=}C^2{-}C^3$ and $C^2{-}C^3{=}O^4$ were depicted.

The calculated data in Table 2 show that $\varphi°_{\text{tBPMAAm}}$ and $\varphi°_{\text{AAm}}$ differ considerably. The torsion angle between the first carbon and oxygen atoms in the carbonyl group is changed to 17.6−22.8°. We assume that the decreased torsion angle minimizes the probability of conjugation in the tBPMAAm molecule. As a result, the $Q_{tBPMAAm}$ value becomes smaller. Remarkably, the torsion angle for the AAm molecule is 180°. It facilitates conjugation and increases the Q_{AAm} value to 1.18. Moreover, the *e* value can be correlated with the dipole moment (μ_x) projection to the double bond.[34] To this end, the smaller *e* value for tBPMAAm in comparison to AAm is in a good agreement with the estimation of the decreased value of μ_x that was calculated for the peroxide monomer molecule (Table 2).

Thus, we assume that large peroxide-containing fragments that hinder multiple bond conjugation and result in a decreased *Q* value are incorporated into the molecule of the peroxide monomer. Furthermore, the smaller value of the projection of the dipole moment for tBPMAAm explains the smaller *e* value for peroxide monomer in comparison to AAm.

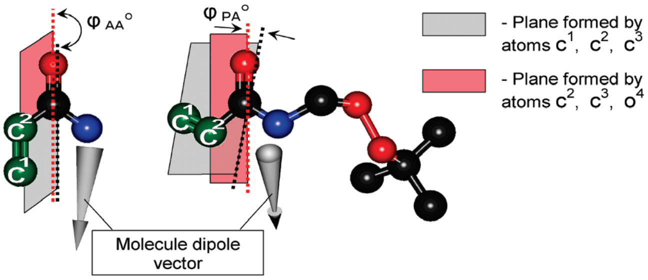


Figure 6. Molecular modeling and comparison of the molecular configurations of tBPMAAm and AAm.

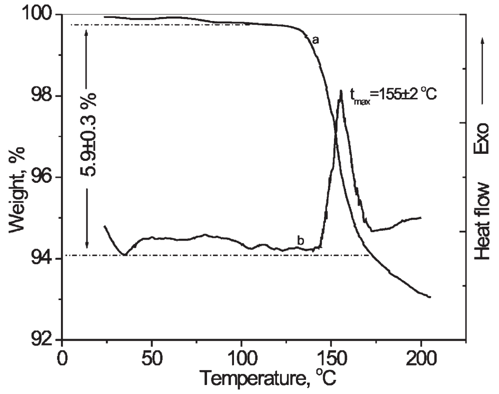


Figure 7. TGA (a) and DSC (b) analyses of tBPMAAm−OMA.

It is important to note that we observed that the ratio of tBPMAAm to OMA fragments in the copolymer determines the properties of the polyperoxide copolymer. Hence, we have found that tBPMAAm−OMA, containing less than 55 mol % of the peroxide monomer, is well soluble in acetone and common aliphatic, aromatic, and chlorinated solvents. Furthermore, tBPMAAm−OMA is sparingly soluble in low molecular weight alcohols. An increase in the peroxide monomer fraction in the copolymer above 55 mol % considerably changes the solubility. The copolymer becomes better soluble in alcohols and less soluble in aliphatic solvents.

To demonstrate the capability of peroxide groups in tBPMAAm−OMA to decompose by heating and initiate radical processes,[35] the thermolysis of the tBPMAAm−OMA composition with a 6.3% mole fraction of tBPMAAm was studied by derivatography.[35] The data shown in Figure 7a clearly indicate the peroxide copolymer sample's weight loss at 130−180 °C. We assume that the weight loss is caused by thermolysis of the peroxide groups. Thermolysis is an exothermic reaction, generating maximum heat at 155 °C (Figure 7b). The observed weight loss for the peroxide copolymer sample (in the range of about 6.5 - 7.5%) correlates with the peroxide group content in tBPMAAm−OMA.

Using experimental derivatography data, the thermolysis reaction order ($n = 1$), activation energy (E_a), and pre-exponential factor (Z) were calculated by modified kinetic eq 1:[36,37]

$$\frac{\mathrm{d}W}{W_{\mathrm{k}}\mathrm{d}t} = \ln\frac{z}{q} - \frac{E}{RT} + n\ln\left(1 - \frac{W}{W_{\mathrm{k}}}\right) \qquad (1)$$

where W = weight loss in mg of the sample at temperature T, W_{k} = total weight loss of the sample in milligrams at a given stage, Z = pre-exponential factor, q = rate of sample heating (°C/s), E = activation energy in kJ/mol, R = universal gas constant, n = reaction order, and T = temperature in K.

Hence, the rate constant eq 1 for tBPMAAm−OMA thermolysis has been determined as follows:

$$K_1 = 2.3 \times 10^{20} e^{(-190 \times 10^3/RT)}$$

Using the rate constant equation, we calculated the half-life of the tBPMAAm−OMA copolymer[35] for different temperatures:

$$\tau_{1/2} = \frac{\ln 2}{K}$$

Thus, at 130 °C, the half-life is 210 min, at 150 °C it is 14 min, and at 170 °C it is 1.3 min. Therefore, it is seen that the kinetic investigations of the new functional polyperoxide permits us to analyze and control the FPP composition and its reactivity in radical processes.

Conclusions

A synthetic way of designing a new acrylamide-based peroxide monomer (*N*-[(*tert*-butylperoxy)methyl]acrylamide) containing a primary−tertiary peroxide group was developed. The peroxide monomer was employed in radical copolymerization with octyl methacrylate to synthesize a new functional polyperoxide (FPP). Monomer reactivity ratios (r_1, r_2) and $Q - e$ monomer activity parameters for copolymerization of the peroxide monomer with octyl methacrylate were experimentally determined. This finding gives researchers control over FPP composition and reactivity in radical processes. The thermal analysis data show that FPP thermolysis is a first-order reaction and indicate a significant polyperoxide decomposition rate at 155 °C. At the same time, the FPP contains functional groups that enable the interaction with a polymeric substrate. To this end, it is expected that the developed FPP will be employed as an efficient surface modifier and macroinitiator of radical reactions. This unique combination of properties makes this new functional polyperoxide promising with regard to polymeric substrate modification.

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References and Notes

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