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Copolymerization of 2,2-Diallyl-1,1,3,3-tetraethylquanidinium Chloride with N-(4-Acetylphenyl)maleimide

Marina N. Gorbunova

Institute of Technical Chemistry Ural Branch of Russian Academy of Sciences, Perm, 614013, Russia

Abstract The free-radical copolymerization of 2,2-diallyl-1,1,3,3-tetraethylguanidinium chloride with N-(4- acetylphenyl)maleimide is studied in bulk and in organic solvents. It is shown that copolymerization in bulk and in solution proceeds to form copolymers with random distribution of monomer units. The kinetic laws of the reaction are investigated, and the relative activities of the monomers are determined. It is found that 2,2-diallyl-1,1,3,3-tetraethylguanidinium chloride is involved in copolymerization with N-substituted maleimides to give rise to pyrrolidinium structures.

Keywords Radical Copolymerization, Quanidinium Salt, N-(4-Acetylphenyl)Maleimide, Kinetics

1. Introduction

Maleimides have found wide use as thermoreactive binders in engineering, electrical insulation, and technical items because materials formed on their basis are resistant to radiation and possess high fire resistance; moreover, their dielectric properties are stable up to 200–250℃[1]. It is known that *N*-substituted maleimides homopolymerize according to the radical mechanism[2,3] and are involved in copolymerization with styrene[4–9], butadiene[4], (meth) acrylic acid and its esters[4,11], vinyl ethers[10–12], and vinylketones[13]. In copolymerization with electron-donor monomers, they, being electron acceptors, form copolymers with a high tendency of monomer units toward alternation[4,9,11,12].

Compounds containing quanidine groups show a broad spectrum of bactericide effects, and they are used as medicines and fungicides[14–16]. That is why quanidine group introduction into high molecular-weight compounds is undoubtedly of interest. 2,2-Diallyl-1,1,3,3-tetraethylguanidinium chloride(AGC) shows promise for this purpose.

The copolymerization of this monomer with *N*-phenyl- and *N*-*p*-carboxyphenylmaleimide was reported in[17]. It was shown that copolymerization proceeds to form copolymers with a high tendency toward alternation of monomer units.

No data is available on the copolymerization of AGC with *N*-(4-acetylphenyl)maleimide; however, the synthesis and characterization of copolymers based on AGC is of great interest since the mentioned compounds can be used in medicine and biotechnology.

In the present study, the copolymerization of AGC with *N*-(4-acetylphenyl)maleimide (APMI) was studied.

2. Experimental

2.1. Materials

2,2-Diallyl-1,1,3,3-tetraethylguanidinium chloride was synthesized as described in[18]. Tetraethylurea (1 mol) was dissolved in dry benzene (2.5 mol). Phosgene was bubbled through the solution at 9-15℃ at the intensive stirring until the reaction was completed (control by gas-liquid chromatography). Then the reactive mixture was heated slowly and was boiled until the gas stopped emanating. It was followed by the cooling of the reactive mixture and dry diallylamine (2.4 mol) was added dropwise with the constant intensive stirring. Then the reactive mixture was stirred for two hours at 50-60℃ and sodium hydroxide (1.2 mol of 50% aqueous solution) was added dropwise to the mixture. After that the reaction mixture was filtered, the filtrate was evaporated under vacuum at 70℃. The obtained AGC was thoroughly rinsed with dry acetone to remove the residual NaCl. Finally, acetone was removed by distillation. The yield of AGC was 70 % from the theory. The purity of AGC was determined via elemental analysis and ^{13C}NMR spectroscopy. According to elemental analysis, the contents of elements are as follows: C, 62.42(calcd., 62.61); H, 10.67(calcd., 10.43); N, 14.58% (calcd., 14.61); and Cl, 12.32% (calcd., 12.35). The chemical shifts (δ, ppm) and multiplicity of the ^{13C}NMR spectrum of AGC are given in Table 1.

* Corresponding author:
mngorb@newmail.ru (Marina N. Gorbunova)
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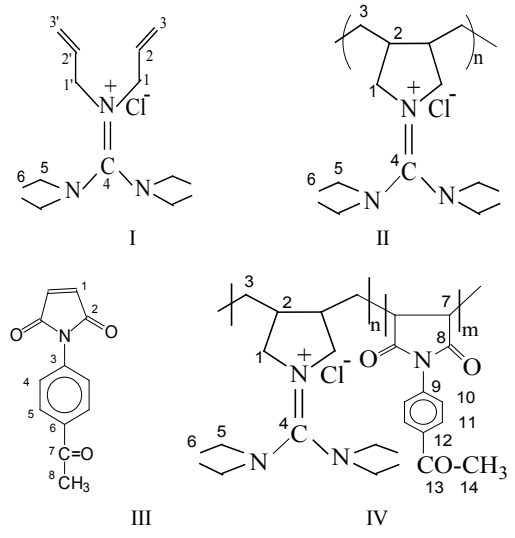
APMI was synthesized as described in[19]; acetone was used as a solvent instead of ether. APMI (T_m = 151-153℃) was used in experiments. According to elemental analysis, the contents of elements in APMI are as follows: C, 67.41 (calcd., 66.98); H, 4.20 (calcd., 4.19), and N, 6.35% (calcd., 6.50). The chemical shifts (δ, ppm) and multiplicity of the 13C NMR spectrum of maleimides are given in Table 1.

The structures of the monomers and polymers are schematically shown on Scheme 1.



Scheme 1. Structures of AGC (I), PAGC (II), APMI (III) and copolymer AGC-APMI (IV)

Initiator AIBN and solvents were purified by conventional methods; their characteristics corresponded to the literature data[20].

2.2. Copolymerization

Copolymerization of AGC with APMI was conducted in bulk and in organic solvents in the presence of $3.0 \cdot 10^{-2}$ mol L^{-1} AIBN. Copolymerization was studied for a molar fraction of AMI from approximately 0.8 to 0.2in the feed. The kinetic investigations were carried out at initial conversions by the gravimetric method at 60-90℃. The reaction was allowed to go on for less than 10% conversion therefore it was terminated stopped at a certain time. Copolymers were precipitated and purified by three-fold reprecipitation by a precipitant (water) from the solution. The purified copolymers were dried under vacuum at 50℃ until constant weight was achieved. The copolymer composition was calculated from the elemental analysis data.

Effective reactivity ratios r_1 and r_2 were calculated via the Mayo–Lewis[21], Finemann–Ross[22], and Kelen– Tüdös [23] methods.

2.3. Measurements

The IR spectra were obtained on a IFS 66/S Bruker spectrometer in KBr tablets.

The ^1H and ^{13}C NMR spectra were recorded on a "Bruker AM-300" spectrometer operating at 300 and 75.47 MHz using a broad-band proton suppression and in a JMOD mode. DMSO-d_6 was used as solvent; tetramethylsilane(TMS) was used as internal standard.

The calorimetric measurements were performed on DSC unit Mettler-Toledo with a scan rate of 10 or 30 ℃·min^{-1}.

The thermogravimetric and differential thermal analyses(TG/DTA) were carried out using TGA/DSC1 unit Mettler-Toledo at the heating rate of 10℃·min^{-1}.

Molecular weight of copolymer was determined by sedimentation method (25°C, (30-40)·10^3 circle/min).

Acute toxicity of the copolymers was measured in mongrel white male mice weighing 18-20 g, using intraperitoneal doses. The mice was injected with these copolymers. The dose was up to 1000 mg·kg^{-1}. Each group consisted of six animals. The animals were observed for 48 h. LD_{50} values were calculated by Prozorovskiy's method[24].

Microbiological tests were performed by serial dilution of preparations in meat-peptone broth followed by inoculation of meat-peptone agar. Test cultures were *Staphylococcus aureus* strain 906, *Staphylococcus saprophyticus*, ATCC 15305, *Micrococcus luteus*, ATCC 4698, *Escherichia coli* strain 25922, *Bacillus subtilis* ATCC 6633, *Salmonella euteriditis, Pseudomonas fluorescens* NCIMB 9046. Bacteria were grown for 20 h or 7 days. Microbial loads were $2.5 \cdot 10^5$ cells in 1 ml of preparation-containing liquid growth medium.

3. Results and Discussion

3.1. Copolymerization of AGC with APMI

The AGC with APMI copolymers were prepared by radical copolymerization in bulk and in DMFA at 80℃ in the presence of AIBN as the radical initiator.

Table 1. NMR ^{13}C spectra of AGC (1), PAGC (2), APMI (3) and copolymer of AGC-APMI (4) (DMSO-d6, TMS, 25C)

		Chemical shift values and signals multiplets of the atoms (δ, ppm)													
	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	C^{11}	C^{12}	C^{13}	C^{14}
I	54.56 t	133.76 d	123.41 t	165.71 s	45.83 t	14.48 k								
II	55.60 t	43.49 d	27.77 t	162.30 s	45.08 t	14.95 k								
III	134,91 д	169,65 s	135,80 s	126,28 d	128,96 d	135,54 d	197.35 s	26,89 s						
IV	52.13 t	47.96 d	43.48 t	172.88 s	41.84 t	13.14 k	51.37 d	174.76 s	136.64 s	126.37 d	127.29 d	128.98 d	197.45 s	26,89 s

The weight average molecular weight of copolymer (66 % mol. APMI) is 37800.

The IR spectra of AGC with APMI copolymer (50 mol% APMI) contain several characteristic bands that are useful to the structural characterization of the polymers. We observe characteristic aliphatic methylene stretches between 3100 and 2850 cm^{-1} and maleimide C=O stretches are seen at 1773 and 1701 cm^{-1}. The broadened carbonyl band at 1701 cm^{-1}in copolymer is the result of spectral overlap between the maleimide C=O stretch and the acetyl C=O stretch.

The structure of the copolymer obtained was investigated using both ^{1}H and ^{13}C NMR. In ^{1}H NMR spectrum of copolymer 2H (CH-CH), 3H (CH_3) of maleimide unit appeared at δ 3.85 (m) and 2.59 (d) ppm, respectively. The peaks observed at δ 3.25 and 1.14 ppm are assigned to protons of $-N(-CH_2-CH_3)_2$ group. The peaks at δ 1.72, 1.58, 1.4 ppm are assigned to protons in pyrrolidinium ring and protons of CH_2 group connected with APMI.

Chemical shift values and signals multiplets of the atoms in ^{13}C NMR spectrum of copolymer is presented in Table 1. The characteristic peaks observed in this study were similar to those for the copolymers obtained by copolymerization of AGC with N-substituted maleimides[17]. The peaks at 26.89 and 197.45 ppm in the spectrum are attributed to the carbons of acetyl group.

As it was shown in[17], AGC and N-substituted maleimides represent monomer pairs with a strong tendency toward radical alternating copolymerization.

Figure 1 shows the composition of copolymers of AGC with APMI versus the composition of initial mixtures.

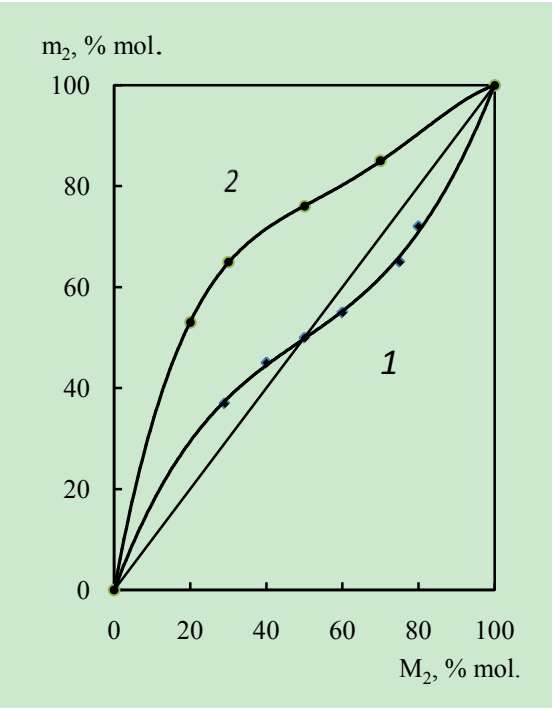


Figure 1. Composition of AGC–APMI copolymers vs. composition of the initial monomer mixture: M_2 and m_2 are the molar fractions of APMI in the initial mixture and in the copolymer. [AIBN] = 0.03 mol/l; *T* = 80°C. *1* - DMFA, [AGC+APMI] = 1.4 mol/l; *2*- in bulk

As it is seen from the diagram of copolymer composition, the activity of maleimide for the reaction in bulk is higher than that in DMFA. As it can be seen, the curve of copolymer composition in DMFA has azeotropic point: the copolymer composition corresponds to the composition of the initial monomer mixture at 50 % mol. APMI. For this system the reactions between dissimilar radicals and monomers occur more easily than those involving similar radicals.

In recent work[17] the maleimides were the more active: $r_{AGC} = 0.07$, $r_{PMI} = 0.14$; $r_{AGC} = 0.03$, $r_{KPMI} = 0.29$. In our case, the monomer APMI is also more active. Effective reactivity ratios for AGC (M_1) and APMI (M_2) are given in Table 2. The reactivity ratios obtained from the three methods are in good agreement within the experimental error.

Table 2. Reactivity Ratios for the Copolymers AGC (M_1) with APMI 80°C, AIBN (3%)

Medium	r_1	r_2	$r_1 r_2$	r_1/r_2
DMFA	0.33±0.03	0.35±0.03	0.116	0.94
In bulk	0.10±0.01	1.68±0.04	0.168	0.06

Comparing PMI, KPMI and APMI to AGC it should be stated that two monomers (PMI and KPMI) show similar copolymerization behaviour. The reactivities of these monomers are close together. There is a question as to whether the para derivative should behave similarly. Due to the presence of the acetyl groups, perhaps, there is a difference at monomer reactivity ratio values of APMI-AGC copolymer. It is shown that copolymerization in bulk and in solution proceeds to form copolymers with random distribution of monomer units.

3.2. Kinetic Regularities of Copolymerization

The study of AGC-APMI copolymerization showed a strong dependence of reaction rate on the monomer ratio. The rate of copolymerization of AGC(M_1) with APMI reduces with the increasing of molar fraction of AGC in the initial monomer mixture(Figure 2).

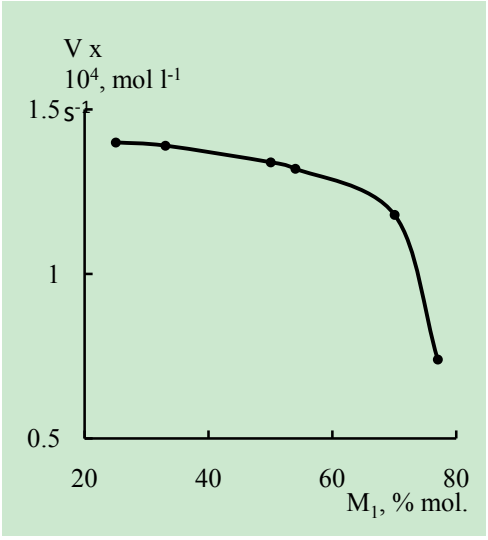


Figure 2. Rate of copolymerization of AGC (M_1) with APMI vs. monomer ratio. DMFA, $[M_1 + M_2] = 1.4$ mol·L^{-1}, [AIBN] = 0.03 mol·L^{-1}, T = 80°C

As a result of kinetic investigations at initial conversions, it was determined that the reaction order of 1/2 with respect to initiator concentration typical for radical polymerization is observed, indicating bimolecular mechanism of the growing chain termination, as well as deficiency of chain transfer to the monomer, typical for allyl monomers. The reaction order with respect to the monomer is 1, which is also characteristic of radical polymerization.

The reaction rate at the studied temperature range (60-90°C) increases with the temperature independently of the medium. The values of the total activation energy of AGC copolymerization with APMI in DMFA, calculated from Arrhenius equation, are 87.0±2.0 kJ·mol^{-1}. This value is in good agreement within the reference data[25] that the values of activation energy of the most reactions of free-radical polymerization are in the range 83.7-96.3 kJ·mol^{-1}.

3.3. Thermal analysis

The thermal behaviour of the synthesized copolymers was investigated by TGA and DSC. It is known that glass transitions of polymaleimides are difficult to observed because they exhibit low changes in heat capacity [26] and are very broad. At heating rate of 10°C min^{-1} the copolymer showed broad scarcely noticeable glass transition. That is why the scan rate of 30°C min^{-1} was used. The T_g values for the AGC-APMI copolymer (66 % mol. APMI) is 222°C (Figure 3). The T_g values for the AGC-APMI copolymers range between 175 and 228°C. T_g of copolymers increases with the APMI content in the copolymer.

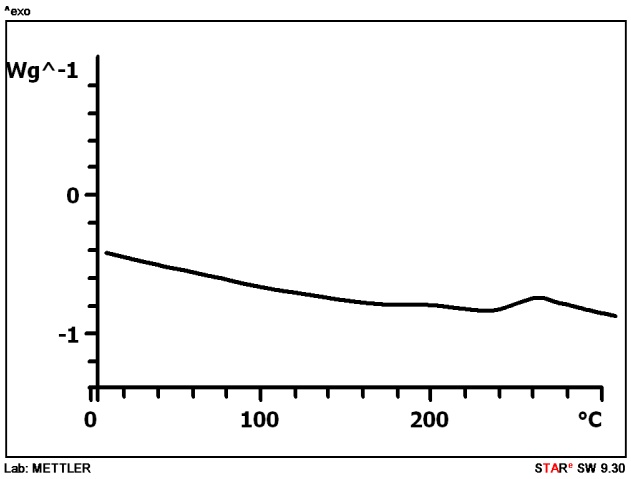


Figure 3. DSC curve of the AGC-APMI copolymer (66 % mol. APMI)

The thermal stability of the AGC-APMI copolymers was studied by thermogravimetric analysis over a temperature range from room temperature to 800°C under air atmosphere at heating rate of 10°C min^{-1} (Figure 4).

Copolymers showed a one-step mass loss process with a slow decomposition process in the range of 220-600°C. The TGA results are summarized in Table 3. It can be seen that the polymers examined are stable at temperatures up to 300°C.

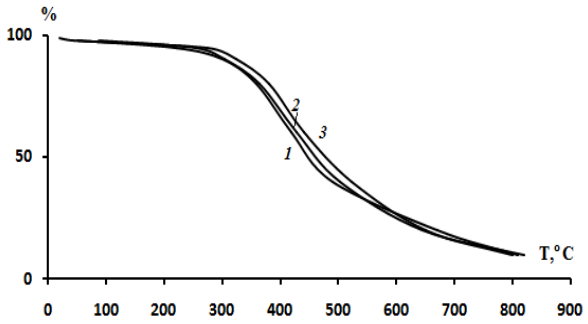


Figure 4. TG curves of the AGC-APMI copolymers: *1* – 37 % mol. APMI; *2* – 52 % mol. APMI; *3* – 52 % mol. APMI

Table 3. TGA Data for the Copolymer

APMI, %mol.	Temperature corresponding to the weight loss (°C)				
	5%	10%	20%	40%	60%
37	220	300	358	419	490
52	255	305	365	429	502
66	280	319	380	434	523

3.4. Biological activity

Antimicrobial agents are defined as those materials capable of killing pathogenic micro-organisms. The great limitations of low molecular weight compounds are based on their residual toxicity even when suitable amounts of the agent are added[27]. The use of antimicrobial polymers prevents the limitation of low molecular weight analogues: reduces the residual toxicity and increases efficiency and selectivity of the agents. Moreover antimicrobial polymers are chemically stable and do not permeate through skin.

Copolymers AGC with APMI were found to be nontoxic (the LD_{50} values were more 1000 mg·kg^{-1}) and therefore could be used for medical purposes. The studies on antibacterial activity showed that copolymer has a pronounced antimicrobial activities with respect to Gram positive microflora. According to the results obtained the minimal bacteriostatic concentration of the copolymer with respect to *Staphylococcus aureus* and *Micrococcus luteus* is observed at 15.6 μg·ml^{-1}, with respect to *Staphylococcus saprophyticus* – at 31.2 μg·ml^{-1} of copolymer.

4. Conclusions

Copolymers of2,2-diallyl-1,1,3,3-tetraethylquanidiniumchloride with N-(4-acetylphenyl)maleimide have been prepared by free-radical copolymerization in dimethylformamide and in bulk at 80°C. The reactivity ratios of the copolymers were estimated using linear graphical Mayo-Lewis, Fineman-Ross and Kelen-Tüdös methods. For the system the r_{APMI} values are higher than the r_{AGC} values this fact confirms the higher reactivity of APMI compared with that of AGC. The TGA results for the copolymers show that they are stable at temperatures up to 300°C. The copolymer obtained has a pronounced antimicrobial activities with respect to Gram positive microflora.

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