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Polymeric Nitrofuran Derivatives. I. Radical-Initiated Homo- and Copolymerization of 5-Nitrofurfuryl Methacrylate

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POLYMERIC NITROFURAN DERIVATIVES. I. RADICAL-INITIATED HOMO- AND COPOLYMERIZATION OF 5-NITROFURFURYL METHACRYLATE

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ABSTRACT

The radical homopolymerization of 5-nitrofurfuryl methacrylate (NFMA) and the copolymerization of NFMA with methyl methacrylate and various vinyl monomers, respectively, have been studied in dimethylformamide at 65°C. NFMA and poly(NFMA) have been characterized by ^{1}H-NMR, IR, and UV spectroscopy. The influence of polymerization conditions on monomer conversion and on the molecular weight of the polymers obtained has been investigated. The thermal behavior of the polymers obtained has been studied by TGA and DSC analysis.

INTRODUCTION

Polymers with a functional group of known antimicrobial activity have received increasing interest as drugs or disinfectants [1, 2]. Carrier-bound disinfectants are formed by covalent bonding of antimicrobially active substances such as organotin compounds or quaternary ammonium compounds to cellulose or crosslinked polystyrene as polymeric carriers [3, 4].

It is known [5] that 5-nitrofuran derivatives are also antimicrobially active. Polymeric nitrofuran derivatives possessing antimicrobial properties were synthesized by modification of natural or synthetic polymers [6–9], but examples for synthesis and polymerization of polymerizable nitrofuran compounds are few [10]. In the present paper the radical-initiated polymerization of 5-nitrofurfuryl

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methacrylate is studied. In addition, the copolymerization of this monomer with methyl methacrylate and other vinyl monomers is also described.

EXPERIMENTAL

Materials

Styrene (ST), methyl methacrylate (MMA), *n*-butyl methacrylate (n-Bu-MA), *n*-butyl acrylate (n-Bu-A), methacrylic acid (MMA), and 2-hydroxyethyl methacrylate (HEMA) were purified by conventional methods. The monomers were freshly distilled under argon before use.

Pyridine was dried by refluxing for 5 h over KOH pellets. Dimethylformamide (DMF) was purified by azeotropic distillation with water and benzene and subsequent distillation over calcium hydride *in vacuo.*

2,2′-Azobisisobutyronitrile (AIBN) was recrystallized three times from dry methanol and dried *in vacuo* at room temperature. 5-Nitrofurfuryl alcohol was prepared by nitration of furfuryl acetate [11], followed by hydrolysis of the nitro ester [12].

Synthesis of 5-Nitrofurfuryl Methacrylate (NFMA)

In a 250-mL three-necked flask under argon were placed 0.20 mol of freshly distilled 5-nitrofurfuryl alcohols and 80 mL dry pyridine. The system was cooled to 10°C, and 0.23 mol of methacryloyl chloride [13] was added dropwise over 20 min. The mixture was allowed to warm up to room temperature and was stirred for 1 h at 60°C. After it had cooled down to room temperature, the reaction mixture was poured into 800 mL ice-cold water. The white precipitate that formed was filtered and dried under vacuum. The crude product was purified by recrystallization from ethanol–water to give the pure methacrylate in 78% yield: mp 52°C.

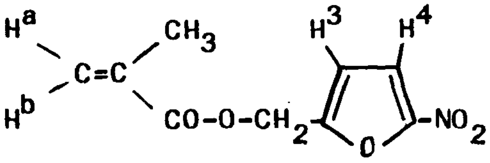
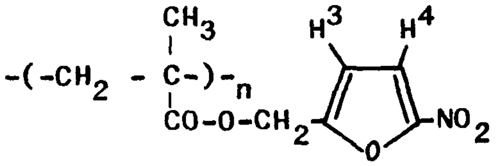
Calculated for $C_9H_9O_5N$: C, 51.19; H, 4.30; N, 6.63%. Found: C, 51.48, H, 4.50; N, 6.52%.

Further characterization was done by ^{1}H-NMR, IR, and UV spectroscopy, and the results are presented in Table 1. The corresponding data are in agreement with the proposed structure.

Polymerization

The polymerization reactions were carried out in sealed glass tubes containing a given amount of AIBN dissolved in DMF. Subsequently, NFMA and comonomer were introduced. The tubes were degassed through three freeze–thaw cycles (liquid nitrogen) before they were placed in a constant-temperature bath (65°C). After a certain time, homopolymerizations and copolymerizations with MMA, n-Bu-Ma, n-Bu-A, and ST were terminated by the addition of excess

TABLE 1. Spectroscopic Data for NFMA and Poly(NFMA)

Spectroscopy		
^1H NMR ($CDCl_3$), δ in ppm	7.22 (CH^4arom.), 6.60 (CH^3arom.) 6.07 (= C$<^{b}_{H}$), 5.58 (= C$<^{Ha}$) 5.13 (–O–CH_2–), 1.88 (CH_3)	7.22 (CH^4arom.), 6.65 (CH^3arom.) 4.96 (–O–CH_2), 2.09–1.51 (–CH_2–) 0.98–0.50 (CH_3)
IR (KBr disk), $\tilde{\nu}$ in cm^{-1}	1720 (C=O), 1640 (C=C) 1515 (as-NO_2), 1355 (s-NO_2)	1735 (C=O), 1500 (as-NO_2) 1350 (s-NO_2)
UV, λ_{max} in nm; ε × 10^4 in $L\cdot mol^{-1}\cdot cm^{-1}$	304; 1.025 (in ethanol)	

methanol. The reaction mixtures of copolymerizations with MMA or HEMA were poured into excess ether. The monomer conversions were calculated from the gravimetrically determined yields of the dried polymers. Poly(NFMA) and poly(MMA-*co*-NFMA) were reprecipitated twice from acetone solutions with methanol and then dried under vacuum at 40°C to constant weight. Copolymer composition was determined by elemental analysis. Poly(NFMA) was characterized by ^{1}H-NMR, IR, and UV spectroscopy (Table 1).

Measurements

^{1}H-NMR spectra were recorded on an KRH-100 R (Academy of Science of GDR) using hexamethyldisilane as the standard. An infrared spectrometer M 80 (VEB Carl Zeiss, Jena) was used to record IR spectra. Ultraviolet absorptions were measured with a spectrometer, Specord (VEB Carl Zeiss, Jena).

The number-average molecular weights of polymers were determined osmometrically. Molecular weight determinations were also done by GPC (commercial Knauer gel chromatograph) by using columns calibrated with polystyrene standards. The eluent was tetrahydrofuran; the temperature was 40°C.

Differential scanning calorimetry (DSC) measurements were performed by using a Perkin-Elmer DSC II thermal analyzer. Scanning rates of 5°C/min were used. Thermogravimetry (TG) of powdered polymer samples was performed with a thermal balance at the heating range of 10°C/min.

RESULTS AND DISCUSSION

Homopolymerization of NFMA

The homopolymerization of NFMA was carried out in DMF at 65°C. The results given in Table 2 demonstrate a clearly lower monomer conversion of NFMA in comparison with that of both MMA and FMA. This observation is in contrast with the fact [14] that other 5-substituted furfuryl methacrylates usually

TABLE 2. Polymerization of Various Methacrylates (2.0 *M*) Initiated by AIBN (0.05 *M*)

Monomer	Time, h	Conversion, %	$\bar{M}_n \times 10^{-3}$ g/mol[a]
MMA	2.0	55.2	16.7
FMA	4.0	87.1	13.7
NFMA	8.0	17.4	2.3
NFMA	24.0	34.0	3.5

[a] Determined by osmometry.

polymerize more rapidly than the unsubstituted one, which can be explained on the basis of a terminating effect of the nitro group. A number of aromatic nitro-compounds are known to act as inhibitors or retarders in the radical polymerization of vinyl monomers [15], but Kice [16] found only a minimal retarding effect of aromatic nitro-compounds in the polymerization of MMA. In order to confirm the influence of nitrofuran compounds on monomer conversion, the polymerization of MMA was carried out in the presence of 5-nitrofurfuryl acetate (NFAc). As shown in Table 3, the monomer conversion and molecular weights of the polymers obtained decreased with an increasing concentration of NFAc, and concentrations of NFAc higher than ~0.50 *M* inhibited the polymerization of MMA. The time–conversion plot of MMA polymerization in the presence of lower concentrations of NFAc is typical for retarders because no inhibition period appears (Fig. 1).

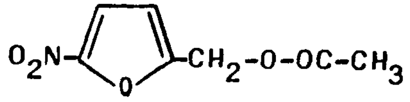
Various mechanisms have been proposed to explain the reaction of nitro compounds with propagating radicals [17]. Unfortunately, the spectra and analyses of the polymers and nonpolymerized monomer fractions obtained did not provide any information that elucidated the mechanism of retardation by nitrofuran compounds.

In the polymerization of NFMA, monomer conversion increases with the time, whereas a decrease of monomer conversion occurs with rising NFMA concentration (Fig. 2). These results confirm that NFMA acted as an autoretarder when it was subjected to free-radical initiation. Therefore, the best polymer yields were

TABLE 3. Polymerization of MMA (2.0 *M*) Initiated by AIBN (0.05 *M*) in the Presence of NFAc[a] (*time*: 2.0 *h*)

[NFAc], mol/L	Conversion, %	$\bar{M}_n \times 10^{-3}$ g/mol[b]
0	55.2	16.7
0.05	34.5	—
0.10	24.7	8.8
0.20	11.3	6.7
0.30	3.1	—
0.50	0	—

[a]NFAc:



[b]Determined by osmometry.

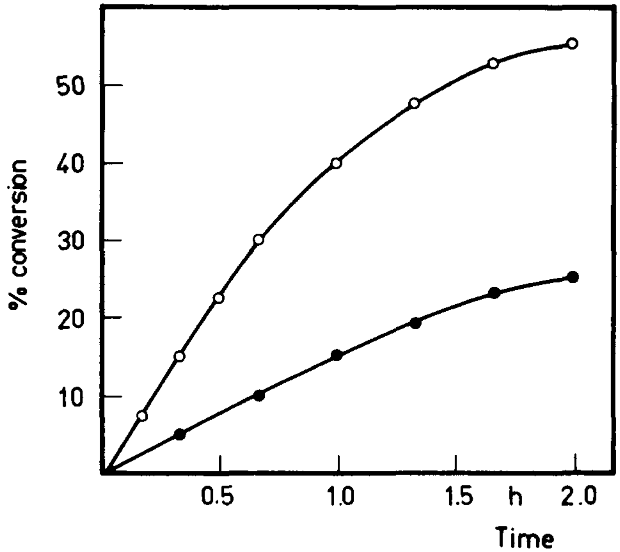


FIG. 1. Polymerization of MMA (2.0 *M*) initiated by AIBN (0.05 *M*) in the presence (●) and absence (○) of 5-nitrofurfuryl acetate (0.10 *M*).

obtained in the presence of low NFMA concentrations and high AIBN concentrations. The molecular weight distributions of NFMA homopolymers obtained by GPC show that the polydispersity of the polymers obtained varies between 1.51 and 1.84 independent of polymerization conditions.

Poly(NFMA) is very soluble in acetone, tetrahydrofuran, and dipolar aprotic solvents, but it is insoluble in hexane, benzene, and methanol. Films can be cast from acetone.

The glass transition temperature of poly(NFMA) ($\bar{M}_n$ = 3500 g/mol) determined by DSC analysis was 74°C. This temperature is lower than the value of 114°C for poly(MMA) ($\bar{M}_n$ = 13 700 g/mol).

The nitrofurfuryl ester function presumably facilitates main chain mobility in comparison to poly(MMA). Figure 3 shows a typical TGA curve of poly(NFMA); for comparison, the thermograms of poly(MMA) are also indicated in this figure. The degradation temperature of poly(NFMA) for a 20% weight loss is 265°C, illustrating that this polymer is somewhat less stable than poly(MMA) and poly(FMA).

Copolymerization of NFMA

The radical copolymerization of NFMA with MMA was carried out in DMF at 65°C. The results in Table 4 and Fig. 4 show that monomer conversion and the

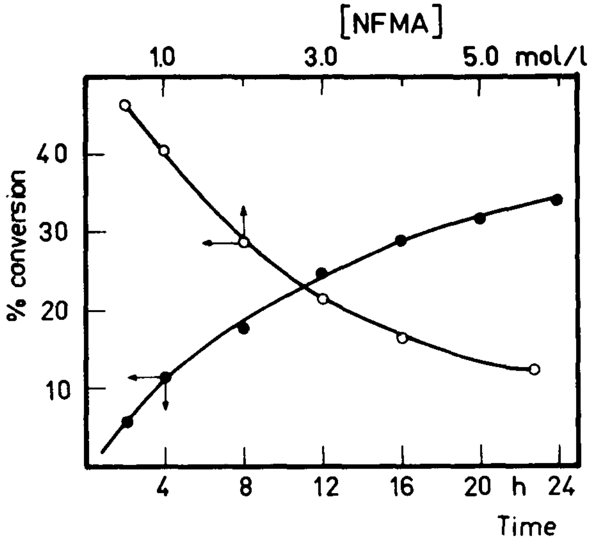


FIG. 2. Polymerization of NFMA initiated by AIBN (0.05 *M*). (○) Time: 16 h. (●) [NFMA] = 2.0 *M*.

molecular weights of the copolymers obtained decrease with increasing content of NFMA in the monomer mixture. This is due to retardation by NFMA. The copolymer compositions were calculated from the nitrogen contents as determined by the Dumas method. ^{1}H-NMR spectroscopy can also be used to determine the copolymer composition. It is advantageous to interpret quantitatively the signals at 4.98 and 3.50 ppm, which correspond to the ($-O-CH_2-$) protons and to the $O-CH_3$ protons in the ^{1}H-NMR spectra of poly(MMA-*co*-NFMA), respectively. Evidently the composition of copolymers can cover a wide range by varying the monomer feed composition. The results of the copolymerization of NFMA and various vinyl monomers are summerized in Table 5. It can be seen that the polymerization of all the monomers used is retarded by NFMA except for styrene which is inhibited. Inhibition of the radical polymerization of styrene by aromatic compounds was also found by Kice [16], and these differences in the behaviors of monomers are attributed to polar factors. Regardless of this, the copolymerization of other monomers with NFMA yielded polymers with pendant 5-nitrofuran groups and different hydrophilicities. In order to clarify the effect of solvent on the copolymerization behavior of NFMA, the copolymerization of NFMA and MMA was carried out in various solvents.

It was found that the monomer conversion in DMF and in DMSO is higher than in benzene or dioxane. In addition, from elemental analysis data of the polymers obtained, it is evident that all the solvents used in the copolymerization experi-

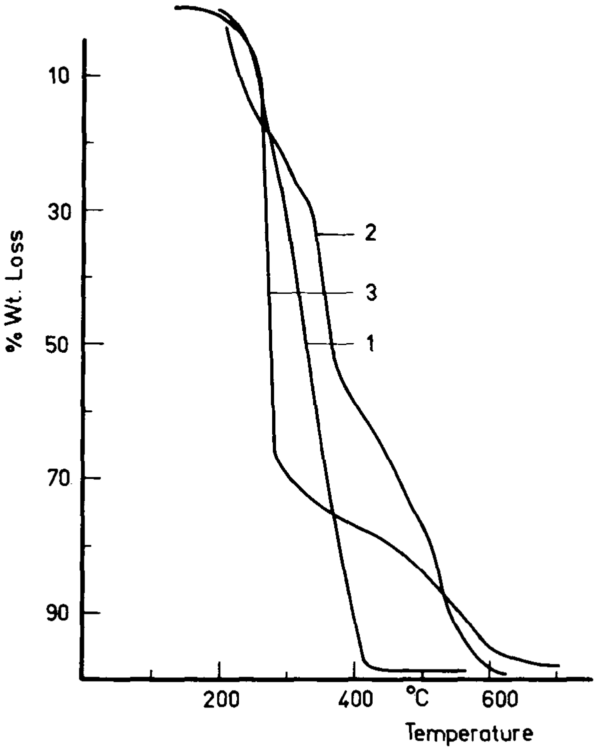


FIG. 3. Thermal gravimetric analysis of poly(methyl methacrylate) (1), poly(furfuryl methacrylate) (2), and poly(NFMA) (3).

TABLE 4. Copolymerization of NFMA and MMA Initiated by AIBN (0.05 *M*). [NFMA] + [MMA] = 2.0 *M* (time: 2.0 h)

f_{NFMA}[a] (feed)	Conversion, %	$\bar{M}_n \times 10^{-3}$ g/mol[b]	Nitrogen content, %	F_{NFMA}[c] (copolymer)
0	55.2	27.0 (16.7)[d]	0	0
0.05	31.5	11.5	0.43	0.03
0.15	16.0	9.7 (7.3)[d]	1.98	0.17
0.25	11.6	6.4	2.93	0.28
0.40	8.8	5.5	3.35	0.33
0.50	7.4	5.2	3.73	0.38

[a] Molar fraction of NFMA in monomer.

[b] Determined by GPC.

[c] Molar fraction of NFMA in copolymer calculated from the nitrogen content.

[d] Determined by osmometry.

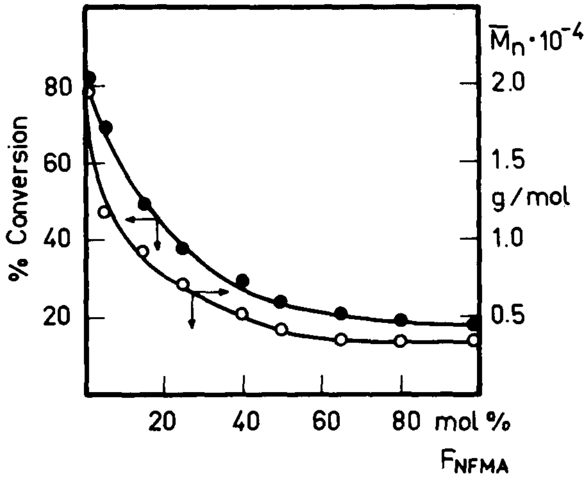


FIG. 4. Conversion and molecular weights (determined by GPC) of MMA-NFMA copolymers as functions of composition (as mol% of NFMA F_{NFMA}). Time: 8 h, [MMA] + [NFMA] = 2.0 *M*, [AIBN] = 0.05 *M*.

TABLE 5. Copolymerization of NFMA with Various Vinyl Monomers Initiated by AIBN (0.05 *M*). [NFMA] + [Comonomer] = 2.0 *M* (time: 6 h)

Comonomer	[NFMA], mol/L	Conversion, %	F_{NFMA}[a] (copolymer)
AN	0.1	80.3	—
	0.3	61.5	0.39
n-Bu-MA	0.1	75.2	—
	0.3	44.6	0.31
n-Bu-A	0.1	71.0	—
	0.3	44.3	0.41
MAA	0.1	86.3	—
	0.3	42.2	0.42
MMA	0.1	67.1	—
	0.3	41.8	0.22
HEMA	0.1	94.2	—
	0.3	58.6	0.37
ST	0.1	0	—

[a] Mole fraction of NFMA of copolymers calculated from the elemental analysis of copolymers.

ments do not have an effect on copolymerization composition. The copolymerization of NFMA and MMA was also carried out in the absence of solvents. In this case, transparent plastic rods of poly(MMA-*co*-NFMA) were obtained.

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