Polymer Bulletin 13, 195–200 (1985)

Polymer Bulletin

Polymeric Herbicides

Biocide Polymers

13.[+] Synthesis and Hydrolysis of Modified Poly(Acrylic Acid)s Containing 3-Amino-1,2,4-Triazole

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SUMMARY

Potential polymeric herbicides have been synthesized by reacting poly(acrylic acid)s with 3-amino-1,2,4-triazole and 1-acetyl-5-amino-1,2,4-triazole, respectively. The produced copolymers contained the active moieties as pendant groups in the range of 3 to 27 per cent of weight and with a content of carboxyl groups up to 95 mol-%. The hydrolytic release of 3-amino-1,2,4-triazole was investigated.

INTRODUCTION

3-Amino-1,2,4-triazole (amitrole) is a well-known herbicide with non-selective activity (1) and has been utilized in the control of weeds, e.g. at road sides and railway tracks (2). However, the application of amitrole is usually restricted due to its high solubility in water. For this reason the reversible attachment to a polymeric carrier (3) offers great promise for enhancing the efficacy of this herbicide. Several examples of the binding of amitrole to synthetic polymers via hydrolytically unstable amide linkages at the amino group or at the ring nitrogen of the active agent have been described recently (4-6). It was the objective of this work to study the reaction of poly(acrylic acid)s and 3-amino-1,2,4-triazole as well as 1-acetyl-5-amino-1,2,4-triazole and to prepare copolymers that contain pendant amitrole amides and carboxyl groups. The results of the study of the hydrolysis and the characterization of these copolymers are also presented.

EXPERIMENTAL

A. Materials

Poly(acrylic acid)s (PAA, M_n = 13,000 and 57,000) were prepared by polymerization of acrylic acid (Merck-Schuchardt) in xylene initiated by dibenzoyl peroxide (7) and potassium

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[+] Part 12: M. Hartmann, H.-J. Bauer, A. Fritzsche and K. Wermann, Makromol. Chem., in press

[++] To whom all communications should be addressed persulfate in water (8) (M_n = 100,000), respectively. Commercially available ethyl chloroformate, triethylamine, and 3-amino-1,2,4-triazole were purified by distillation and recrystallization (acetonitrile), respectively. 1-Acetyl-5-amino-1,2,4-triazole was prepared from 3-amino-1,2,4-triazole in 85% yield using acetyl chloride in THF at 0 °C (9). Phenyl N-phenylphosphoramidochloridate was obtained as described previously (10). DMF was dried by standard methods and distilled in vacuo.

B. Techniques

The molecular weights of poly(acrylic acid)s were calculated from the intrinsic viscosity (13). The viscosities of the polymer solutions were measured in 2N NaOH at 25 °C by using a SEIDE-DECKERT viscometer. ^{1}H-NMR spectra were recorded on a KRH-100 R spectrometer (ZWG of the AdW of GDR) using [$^2H_6$]-DMSO solution and hexamethyldisilane internal standard. IR spectra in KBr pellets were recorded on a spectrometer UR 20 and the spectrophotometric determination of amitrole was carried out on a Spekol equipped by EK 5 (both Kombinat Carl Zeiss Jena).

C. Procedures

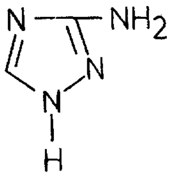
Reaction of 3-amino-1,2,4-triazole and 1-acetyl-5-amino-1,2,4-triazole with PAA

To a solution of PAA (1.8 g, 25 mmole) in DMF (50 ml) triethylamine (2.5 g, 25 mmole) and ethyl chloroformate (2.7 g, 25 mmole) were added successively at -8 °C (11). After 1 hour of stirring at -8 °C a cooled solution (-8 °C) of 3-amino-1,2,4-triazole in 10 ml DMF was added dropwise. Stirring was continued at -8 °C for an additional hour and then at room temperature for 16 h. A corresponding procedure was carried out with 1-acetyl-5-amino-1,2,4-triazole (25 mmole). Equivalent amounts of phenyl N-phenylphosphoramidochloridate can be used for activation of PAA at room temperature.

The reaction mixture was filtered and the products were precipitated into methanol (600 ml) and filtered off. After repeated reprecipitation from DMSO/methanol, the products were extracted with diethyl ether in a Soxhlet extractor for 30 h and dried under vacuum at room temperature. Details of amidiation experiments are shown in Table 1.

Hydrolysis Studies

Samples of each copolymer containing 10 - 20 mg of covalently bound amitrole (particle size 0.063 - 0.200 mm) were magnetically stirred in 250 ml bidistilled water (pH 5.9) in a hydrolysis apparatus. The reaction mixture was kept at 30 °C in a constant temperature bath. Samples of 5 ml were removed from the solution through a filter appliance in appropriate periods, and an equivalent volume of water was returned. This change of concentration was taken into consideration in quantitative analysis. The amount of amitrole released from each copolymer was determined by spectrophotometric analysis using trisodium pentacyanoaminoferrate according to the method of LaRue (12) (λ_{max} = 532 nm, ε = 4550 l cm^{-1} mol^{-1}).



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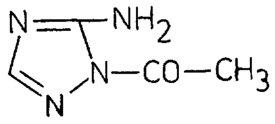

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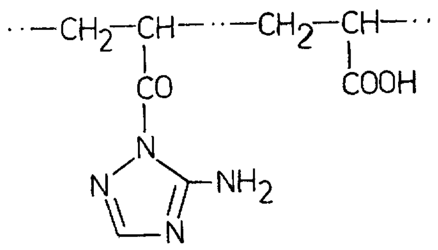

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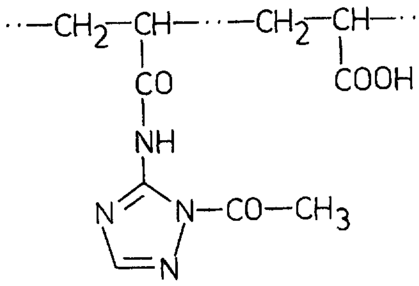

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RESULTS AND DISCUSSION

Acrylic polymers (3a, 3b, 3c and 4a, 4b, 4c) have been synthesized from poly(acrylic acid)s (PAA) having various molecular weights and 3-amino-1,2,4-triazole (1) or 1-acetyl-5-amino-1,2,4-triazole (2) in the yield of 85 - 92% (Table 1). In order to increase the reactivity of PAA, ethyl chloroformate was used to form mixed anhydride groups that reacted with the heterocyclic amines at -8 °C. Similar results were obtained when the reaction was carried out with phenyl N-phenylphosphoramidochloridate.

It was found that the achieved degrees of substitution are independent of the molecular weights of PAA and could not be increased by variation of the amount of added 1 and 2, respectively. As shown in Table 1, the reaction of 2 with activated PAA gave copolymers containing only 3 - 5 mole-% amitrole as pendant groups, whereas by the analogous reaction of 1 some 30 mole-% of the active agent could be linked. This different behaviour is due to the higher reactivity of the ring-NH bond compared with the primary amino group of amitrole and is in accordance with the results of corresponding acylation reactions using low molecular weight acid derivatives (9).

Table 1: Reaction of 1 and 2 with PAA activated by ethyl chloroformate

copolymer[1)]	yield (%)	N-content (%)	polymer composition acrylic acid units (mole-%)
3a	89	17.88	70.9
	92[2)]	15.80	75.0
3b	85	16.16	74.3
3c	85	16.73	73.2
4a	90	3.48	95.2
	90[2)]	2.10	97.2
4b	87	5.07	92.8
4c	87	5.09	92.7

[1)] Obtained from PAA with molecular weights of 100,000 (3a, 4a), 57,000 (3b, 4b) and 13,000 (3c, 4c)

[2)] Phenyl N-phenylphosphoramidochloridate was used for activation of PAA

The data of the IR spectra and the typical ^{1}H-NMR chemical shifts of the copolymers 3 and 4, respectively, demonstrate that the triazole group in the copolymers 3 is attached to PAA via the heterocyclic N(2) atom forming an azolide linkage. On the other hand the occurrence of NH deformation vibration (amide II band) and the absence of typical values for the ^{1}H-chemical shift of the amino group in the spectra of the copolymers 4 indicate linkage through the primary amino group. Furthermore, both copolymers exhibit the resonance of the CH protons of the triazole ring in positions three and five, respectively, at δ= 7,40 and 7,87 ppm (14, 15).

Table 2: Characteristic data of the IR and ^{1}H-NMR spectroscopy of the copolymers 3 and 4

copolymer	IR data [cm^{-1}]			^{1}H-NMR data [ppm]		
	$\nu_{C=O}$ (amide I)	$\nu_{C=O}$ (acid)	δ_{NH} (amide II)	δ_{CH} (ring)	δ_{NH_2}	δ_{CH_3} (acetyl)
3	1700	1730	-	7.40(H^3)	7.90	-
4	1700	1730	1530	7.87(H^5)	-	1.08

In our previous paper (6) we have described the synthesis of polymers that contain amitrole as pendant groups and possess various hydrophobicities. Preliminary hydrolysis studies suggest that the release of the active agent may be modified by changing the nature of the herbicide-to-polymer amide linkages, but complete release occurred only slowly. The copolymers 3 and 4, however, are expected to release the herbicide faster due to their hydrophilicities and the neighbouring carboxyl group participation in the hydrolysis. Results of the hydrolysis studies are summarized in Table 3, in which the times for 50 per cent and 100 per cent release of bound amitrole are listed. It is obvious from these data that the copolymers 4 were hydrolyzed more slowly than the copolymers 3 in spite of the increased content of carboxyl groups. Consequently, the more unstable triazolide bonds in the copolymers 3 contribute most to the ease of hydrolysis in bidistilled water as well as in water at pH 3 and 9.18 and in dilute potassium chloride solution.

Table 3: Hydrolytic release of amitrole from acrylic copolymers 3 and 4 at 30 °C.

copolymer[1]	bidist. H_2O		pH 3.0		pH 9.18		0.1 N KCl	
	t_{50}	t_{100}	t_{50}	t_{100}	t_{50}	t_{100}	t_{50}	t_{100}
	(h)		(h)		(h)		(h)	
3a	1.0	7.8	0.3	0.8	0.3	0.8	0.8	2.0
3b	0.1	2.3	0.1	0.4	0.1	0.4	0.3	1.2
3c	0.1	2.0	0.1	0.4	0.1	0.4	0.1	0.8
4a	65.0	189.0	0.4	3.0	0.5	3.5	14.0	51.5
4b	50.0	189.0	0.5	3.0	0.4	3.0	9.3	25.5
4c	34.0	170.0	0.5	3.0	0.4	3.0	9.3	24.0

[1] cf. Table 1

As shown in Table 3 an insignificant dependence of the hydrolysis rates upon molecular weights could be observed. Since surface effects may also influence the release of the covalently bound agent in heterogeneous medium, kinetic data have not been determined up to now.

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Accepted March 14, 1985