NOTES

On the Possibility of Obtaining Polymeric Materials With Herbicidal Activity

The possibility of obtaining copolymers of acrylamide with 12 derivatives of 1,3,5-triazine, containing an allyl group and showing herbicidal activity is studied. Blends of 6 of these compounds and partially hydrolyzed PAN (produced in Bulgaria and applied in agriculture as a soil conditioner) combine the herbicidal activity of triazine derivatives and polymer properties, revealing a synergistic effect as well.

INTRODUCTION

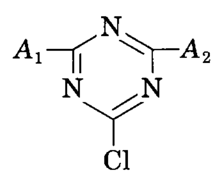
The conventional methods for application of pesticides in agriculture represent a dangerous source of contamination of the environment and are hazardous, not only for the working personnel, but also for the neighboring areas and for underground water. These facts have led to a search for more acceptable methods from the ecological point of view, by introduction of pesticides through polymeric forms—copolymers, polymer blends, microencapsulation etc.[1-4] The application of pesticides in polymer form offers some very important ecological advantages, like working with water solutions instead of spreading dusts or suspensions, limitation of their penetration into underground water or blowing off to the neighboring plots of land and the possibility for their application in the form of foil or ribbon on the respective piece of land.

Obtaining herbicidal active polymers by copolymerization of monomers, one of which is a herbicide, requires the presence of suitable functional group in its molecule.

The 1,3,5-triazine derivatives are well-known and widely applied herbicides in agriculture. The molecular structure of triazines offers substantial possibilities for modification of the properties by substitution of one or two of the substituents conventionally applied. Following this idea we have synthesized triazine derivatives: dyes,[5,6] fluorescent whitening agents,[7] and stabilizers[8] for polymeric materials. They have one or two unsaturated groups in their molecule, enabling them to copolymerize, thus chemically colored resp. bleached or stabilized polymers were obtained. It was of interest to check the same possibility for triazine herbicides. We synthesized a group of new unsaturated triazine derivatives comprising 1 or 2 allyl groups in their molecule, which have very good herbicidal and bactericidal (against some phytopathogenic bacteria) activity.[9,10] The presence of such groups offers the possibility of participation of these compounds in copolymerization processes. It was of interest to study this possibility and to examine the properties of the polymers thus obtained.

Another approach to the preparation of ecologically friendly pesticides consists of application of polymer blends. This possibility is also investigated in the present study.

Triazine derivatives with the general formula 1 were investigated, where A_1 is an aliphatic amino residue or chloroaniline while A_2 is $-NHCH_2CH{=}CH_2$ or $-OCH_2CH{=}CH_2$



(1)

EXPERIMENTAL

Materials

The triazine derivatives of the general formula 1 are synthesized, according to a method already described.[9] Acrylamide (ACA), Fluka, p.a.; Silicagel plates (Fluka F_{60} 254) 20 × 20 cm, 0.2 mm; n-heptane, acetone, dimethyl sulfoxide (DMSO), and methanol-for analytical or spectroscopic purposes.

Polymerization of Acrylamide[11]

A solution of ACA (10 g) in distilled water (80 mL), containing potassium persulfate (0.186 g) is introduced into a flask equipped with facility for flushing with nitrogen, and placed in a thermostat. The respective triazine derivative (0.01 g) dissolved in DMSO (5 mL) is added to this solution. The temperature of the mixture is kept constant

Journal of Applied Polymer Science, Vol. 54, 2187–2190 (1994)
 CCC 0021-8995/94/132187-04

at 45°C for 3 h and then the polymer obtained is isolated by precipitation in acetone. The polymer is dissolved in water and precipitated with acetone (a suitable solvent for triazine compounds) several times until the filtrate becomes free of triazine monomer (thin layer chromatography monitoring on silicagel plates using a system of *n*-heptane : benzene : methanol = 2 : 4 : 0.5 as eluent). The polymers thus treated are dried under reduced pressure at 30°C to constant weight.

Analysis of Polymers

Elemental analysis—performed at the Center of Specialty Polymers, Sofia; IR spectra—recorded in KBr pellets on a Perkin–Elmer spectrophotometer: $\bar{\nu}_{C=N}$: 1540–1620 cm^{-1} and $\bar{\nu}_{C-Cl}$: 950–980 cm^{-1}.

Preparation of blends with "Modipan:" (PAN, partially hydrolyzed in an alkaline medium). The respective triazine compound (0.1 g, dissolved in about 5 mL of DMSO) is added to 10% aqueous solution of "Modipan" (1 kg). The mixture is homogenized in an ultrasonic bath at room temperature; before the analysis the mixture is diluted with water (1 : 10).

Physiological Tests

Physiological tests were carried out under the same conditions as those for testing of triazine derivatives, observing officially accepted Bulgarian requirements (Tzibulska's test).[12] Standards used were seeds of wheat (sort "Sadovo-1") and of cucumber (sort "Bistrenski"). Each sample contained 50 seeds treated with water solutions of respective polymers (concentration 8 mg/L) and were placed on Petri dishes which were kept in the dark for 96 h at 25°C. After this time lapse, we measured the length of their roots (1). These data have been statistically developed and were related to those for the seeds treated with solution of pure polyacrylamide (PAC), according to formula 2

$$l/lo \times 100\ [\%] \tag{2}$$

The lower the value, the higher is the activity of the product (suppression of growing). These results are presented in Table I.

Soil Conditioning Tests

These studies were carried out observing the requirements of a method, accepted (standardized) in Bulgaria[13] as follows: 50 g of soil, treated with 1 wt % water solution of the corresponding polymer blend, was tested by the "wet" method, using five types of sieves (3, 2, 1, 0.5, and 0.25 mm).[13] Using determination of the weight of each fraction, the percentage of different water-stable aggregates has been calculated. The data thus obtained were compared with those for the soil untreated with polymer.

RESULTS AND DISCUSSION

Twelve triazine derivatives of the general formula 1 were studied. The meanings of A1 and A2 are given in Table I. Acrylamide was chosen as a suitable monomer because it's polymers are water-soluble and find practical appli-

Table I Physiological Action of Acrylamide Copolymers with 1,3,5-Triazine Derivatives with Formula 1

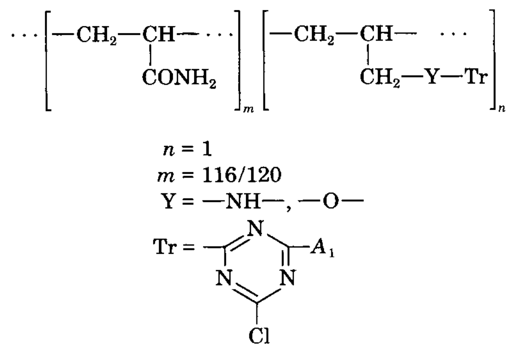
Comp. No.	A_1	A_2	Action[a] [%] Wheat	Action[a] [%] Cucumber
1	$-N(CH_3)_2$	$-NHCH_2CH{=}CH_2$	48	51
2	$-N(C_2H_5)_2$	$-NHCH_2CH{=}CH_2$	50	54
3	$-NHC_2H_5$	$-NHCH_2CH{=}CH_2$	51	66
4	$-NHCH(CH_3)_2$	$-NHCH_2CH{=}CH_2$	83	51
5	$4-Cl-C_6H_4-NH-$	$-NHCH_2CH{=}CH_2$	33	25
6	$2,4-diCl-C_6H_3NH-$	$-NHCH_2CH{=}CH_2$	43	33
7	$-N(CH_3)_2$	$-N(CH_2CH{=}CH_2)_2$	46	89
8	$-N(C_2H_5)_2$	$-N(CH_2CH{=}CH_2)_2$	43	105
9	$-NHC_2H_5$	$-N(CH_2CH{=}CH_2)_2$	46	85
10	$-NHCH(CH_3)_2$	$-N(CH_2CH{=}CH_2)_2$	45	60
11	$4-Cl-C_6H_4-NH-$	$-N(CH_2CH{=}CH_2)_2$	68	37
12	$2,4-diCl-C_6H_3-NH-$	$-N(CH_2CH{=}CH_2)_2$	47	39

[a] Action (suppression of seed growth) = $l/l_0 \times 100$ where l is length of the roots for seeds treated with copolymer, and l_0 resp. for the seeds treated with homopolymer.

cation. Polymerization takes place under mild conditions in aqueous medium.

Water-soluble acrylamide copolymers are obtained with all 12 triazine derivatives. After several precipitations for the removal of unreacted monomers, investigations were carried out to demonstrate and confirm the herbicide-polymer chemical bond.

The elemental analysis data suggest a triazine derivative-to-acrylamide unit molar ratio of 1 : 116(120), as shown in formula 3:



(3)

The infrared (IR) spectra of the reprecipitated copolymers reveal bands characteristic of the triazine monomers which are not observed in the spectrum of homopolyacrylamide. On the basis of our experimental results the conclusion can be drawn that copolymers of acrylamide and triazine compounds are actually obtained.

Data on physiological tests of the reprecipitated copolymers are shown in Table I, where the activity is expressed by the ratio between the length of the roots of seeds treated with copolymer and with homopolyacrylamide only (l/lo × 100). According to the test, the lower the value of this parameter, the higher is the activity, because suppression of growth is greater.

It is seen that all copolymers show physiological activity and this is a promising possibility for their application in agriculture.

Another possibility for application as pesticides can be found in the combination of a physical matrix or a polymer blend. The polymer "Modipan" is produced in Bulgaria from PAN wastes. Modipan is, in fact, partially hydrolyzed PAN and finds application as a soil conditioner in agriculture. The possibility of combined application of a herbicide and a soil conditioner is also checked in order to establish whether the two components preserve their properties after blending.

Copolymer blends are prepared using compounds No. 7–12 (10% aqueous solutions) in a ratio of 99 : 1 and physiological tests are carried out according to the methods described.[12] The data obtained are presented in Table II. It should be noted that the action of the blends on wheat is higher than that established with the mixture of Modipan and the commercial product Atrazine. In fact the polymer blends show very good selectivity with respect to the two vegetable types, which is several times higher than that of the pure monomeric triazine compounds. The explanation of this synergistic effect of the polymer and the unsaturated triazine derivatives will be the object of our future investigations. Tests on the polymeric blends showed no change of their soil conditioning properties in comparison with these of the Modipan (the main part of the soil's fractions are with diameter between 1–2 mm), which is accepted to be good enough for the soil conditioner. In summary, the following conclusions can be drawn:

(a) Unsaturated triazine derivatives copolymerize with acrylamide and the resulting copolymers show herbicidal activity.

(b) The blends of triazine derivatives and partially hydrolyzed PAN (Modipan) show very good herbicidal activity and high selectivity, combining the herbicide with soil conditioning properties.

Table II Physiological Action of "MODIPAN" Blends with 1,3,5-Triazine Derivatives of Formula 1

Comp. No.	Action[a] [%]		Selectivity	
	Wheat	Cucumber	Pure Compounds	Polym. Blend
7	10	45	1 : 1	1 : 4
8	0.3	42	1 : 1	1 : 140
9	0.3	14	1 : 1.6	1 : 48
10	3	50	1 : 1.5	1 : 18
11	3	23	1 : 6	1 : 8
12	1	12	1 : 3	1 : 10
At[b]	8	22	1 : 1.2	1 : 3.5

[a] Action (suppression of seed growth) = $l/l_0 \times 100$: where l is for the seeds treated with polymer blend, and l_0 – with water.

[b] At = blend of Modipan with "Atrazine" commercial product of Bulgaria.

The authors would like to thank to Bulgarian Foundation "Scientific Research" for the financial support of these investigations.

References

1. N. Cadarelli, *Adv. Pesticide Sci.,* 4th Congress, Zurich, 1978.
2. N. Mefarlane, *Pest. Sci.,* **9**(5), 411 (1978).
3. J. Vartiak and G. Worteley, U.S. patent no. 4076516 (1978).
4. *Preparation Forms of Pesticides,* Nitechim, Moskwa, 1984, p. 42.
5. T. Konstantinova, A. Draganov, Hr. Konstantinov,

and Vl. Kabaivanov, *J. Appl. Polym. Sci.,* **16,** 725 (1972).
6. T. Konstantinova, A. Draganov, and Hr. Konstantinov, *Die Angew. Makrom. Chemie,* **43,** 29 (1975).
7. T. Konstantinova and I. Grabchev, *Die Angew. Makrom. Chemie,* **196,** 107 (1992).
8. T. Konstantinova, A. Bogdanova, S. Stanimirov, and Hr. Konstantinov, *Polym. Degrad. Stability,* **43,** 187 (1994).
9. T. Konstantinova, *Compt. rendus de l'Acad. Bulg. des Sci.,* **41**(10), 69 (1988).
10. T. Konstantinova and N. Bogatzevska, 7th International Congress *Plant Pathogenic Bacteria,* Budapest, 1989.
11. W. Sorenson and T. Cambell, *Preparative Methods of Polymer Chemistry,* Interscience Publishing Inc., New York, 1962, p. 220.
12. T. Tzibulska, *Plant Physiol.,* **2**(2), 18 (1984) (Russian).
13. *Practicum for Soil,* J. Kauritchev, ed., Colos Publishing, Mockow-1973, p. 91 (Russian).

T. KONSTANTINOVA*
L. METZOVA

Higher Institute of Chemical Technology,
Chair of Organic Synthesis Technology,
Sofia 1756,
Bulgaria;

HR. KONSTANTINOV

Research Center for Specialty Polymers,
Sofia 1756,
Bulgaria

Received January 26, 1994
Accepted February 27, 1994

* To whom correspondence should be addressed.