Photoinitiated Graft Copolymerization of Glycidyl Methacrylate and 2-Hydroxyethyl Methacrylate onto Polyacrylonitrile and Application of the Synthesized Graft Copolymers in Penicillin–Amidase Immobilization

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SYNOPSIS

The photoinitiated graft copolymerization of hydroxyethyl methacrylate and/or glycidyl methacrylate onto polyacrylonitrile (PAN) and the applicability of the matrices synthesized in this way for penicillin–amidase immobilization are discussed. The copolymers are prepared by putting irradiated PAN fibers with preliminary adsorbed benzophenone on them into the polymerization feed that includes hydroxyethyl methacrylate and/or glycidyl methacrylate dissolved in a water–methyl ethyl ketone mixture. The degree of grafting varies between 11.7 and 46.0%, and its efficiency, between 27.8 and 78.9%. The concentration of epoxy groups in the synthesized copolymers is in the range between 210 and 2220 μmol/g. The reactivity ratios of the two comonomers are determined to be $r_{GM} = 0.70 \pm 0.15$ and $r_{HEMA} = 2.73 \pm 0.14$. The grafted copolymers containing HEMA units provide milder conditions for penicillin–amidase covalent binding. The optimum pH and temperature values of penicillin–amidase immobilized on these matrices are 7.5 and 45°C, respectively. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Graft copolymerization onto polyacrylonitrile (PAN) has not been fully investigated yet.[1] No data have been found concerning the grafting of glycidyl methacrylate (GM) and 2-hydroxyethyl methacrylate (HEMA) onto PAN. The chemical inertness of PAN and the ability of the GM epoxy groups to interact with amino groups in a wide pH interval at room temperature[2–5] make possible the application of the GM grafted onto PAN for enzyme and cell immobilization. The influence of the photoinitiated graft copolymerization conditions on the degree and efficiency of grafting are studied. Penicillin–amidase is an enzyme used at the industrial scale in the production of 6-aminopenicillanic acid and 7-aminocephalosporanic acid. Various methods of penicillin–so far: adsorption,[6,7] adsorption–reticulation,[8] gel entrapment,[9,10] covalent binding,[11–18] and reticulation of soluble enzyme.[18] Oxirane matrices are some of the most commonly used carriers of covalently bound PA, but copolymers of GM grafted onto PAN have not been used for that purpose yet.

EXPERIMENTAL

Materials

To obtain a suitable column filling containing immobilized PA, PA fibers (Nephtochim-Co, Bulgaria) 0.1 mm in diameter and 2.5–3 mm in length were used after being washed for 10 h in acetone. GM (Fluka), HEMA (BDH, Chemicals, Ltd), benzophenone (Riedel de Haen, Germany), benzylpenicillin potassium salt (Antibiotics-Co, Bulgaria), and PA enzyme preparation (Olaina, Latvia) having 1700 U/g activity were used without further purification.

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Methods

Photoinitiated Graft Copolymerization

A three-stage procedure for photoinitiated grafting of GM onto polypropylene suggested in a U.S. patent[19] was followed in this experiment after being modified. The first stage was adsorption of benzophenone (an effective photosensitizer) on PAN fibers during 2 h in a 0.55% solution of benzophenone (BPh) in acetone at 75°C. The mass ratio BPh/PAN was 0.1. PAN fibers thus treated were vacuum-dried to constant weight at 40°C. The second stage was irradiation of PAN fibers with adsorbed BPh on them with unfiltered UV light (a mercury source Narva-125 with power of 45 or 125 W, Germany) for 10 min. The samples were situated in quartz tubes with air or argon atmosphere at a 10 cm distance from the UV source. The third stage was the grafting itself. It included pouring of 20–40 mL GM or GM and HEMA solution on 0.5–1.0 g irradiated fibers with adsorbed sensitizer on them (the mass ratio PAN/monomer was changed from 0.16 to 0.65). A solvent mixture consisting of methyl ethyl ketone (MEK), water, and dimethylformamide (DMF) was used. The volume concentration of MEK varied between 25 and 84.6%; of water, between 7.7 and 20%; and of DMF, between 0.0 and 35.0%. In all cases, 2×10^{-3} M ferrous sulfate was added to the solvent mixture. It increases the efficiency of graft copolymerization.[20] The grafting was carried out at 75°C for 4 h (in the nonkinetic experiments). The ungrafted homo- and copolymers were washed out by acetone extraction in a Soxhlet apparatus for 20–24 h. It had been previously determined that if the acetone extraction of the homopolymer exceeds 15 h the mass of the grafted copolymer stopped changing and the extract was free of polymer.

The degree (D) and the efficiency (E) of the graft copolymerization were determined gravimetrically by the following equations:

$$D(\%) = \frac{g_1 - g_2}{g_2} 10^2 \quad (1)$$

$$E(\%) = \frac{g_1 - g_2}{g_1 - g_2 + g_3} 10^2 \quad (2)$$

where g_1 is the mass of the grafted copolymer; g_2, the mass of the PAN matrix, before grafting; and g_3, the mass of the washed-out polymer.

If the side chains in the matrix consist of GM only, and if the concentration of the epoxy groups (C_{EG}) is known, the value of D can be calculated according to the equation

$$D(\%) = \frac{C_{EG}142 \times 10^{-4}}{1 - C_{EG}142 \times 10^{-6}} \quad (3)$$

where 142 is the molecular weight of the GM monomer unit.

Determination of the Epoxy Group Concentration in the Grafted Copolymer

The epoxy group surface concentration was determined by the method presented in Ref. 21. It had been previously determined that the hydrochlorination of the epoxy groups (EG) in the grafted copolymer was completed within 22–24 h.

SPR Spectra Registration

Samples of pure BPh and of BPh adsorbed on PAN were put in SPR tubes. One group of them was saturated with argon. The plugged tubes were irradiated by UV light. At certain intervals, the SPR spectra of the samples were recorded by Bruker RR-440 SPR spectrophotometer.

Immobilization of PA

Twenty milliliters of PA solution in 0.1 M phosphate buffer (pH 7.5) with an activity 100 U/mL was added to 1 g of grafted copolymer. After a short stirring time, the suspension obtained was left for 72 h at room temperature.[3] The suspension was filtered through a glass filter G2 and washed several times with the same buffer until there was no activity registered in the wash waters.

PA Activity Determination

The enzyme activity that produces 1 μmol of 6-aminopenicillanic acid per 1 min as a result of the hydrolysis of a 0.016 M solution of benzylpenicillin potassium salt in 0.1 M phosphate buffer (pH 7.5) at 40°C is defined as an activity unit (1 U). The enzyme activity of PA was determined iodometrically.[22]

RESULTS AND DISCUSSION

Degree and Efficiency of Grafting

Table I presents the values of D and E of grafting, carried out in different solvent mixtures. It also includes values of C_{EG} related to D. The first important conclusion follows from a comparison of the results

Table I Epoxy Group Concentration (C_{EG}), Degree (D), and Efficiency (E) of Grafting of Copolymers, Synthesized at Different Compositions of the Reaction Feed; Time 4 h; Temperature 75°C

	Copolymerization Feed							
N	C_{GM} (%)	C_{MEK} (%)	C_{H_2O} (%)	C_{DMF} (%)	C_{HEMA} (%)	D (%)	E (%)	C_{EG} (μmol/g)
1	7.70	84.60	7.70	0	0	46.0	74.5	2220
2	20.00	25.00	20.00	35.00	0	11.7	27.8	742
3	3.85	84.60	7.70	0	3.85	39.3	78.9	210

from experiments 1 and 2 (Table I). DMF is an undesirable component of the solvent blend because when it is found in the reaction feed (example 2) the smallest values of D, E, and C_{EG} are obtained in spite of the greatest GM concentration. To explain these essential differences between the D, E, and C_{EG} values, the mechanism of the initiation of graft copolymerization must be known and it is not thoroughly elucidated yet.[23,24]

BPh was used for the first time by Oster and Shibata[25] as a sensitizer during the initiation of polymerization processes. Later, it was widely applied in the generation of active centers on different polymers.[26-29] The mechanism of BPh action is explained by contradictory hypotheses. In Ref. 23, the primary act of generation of active centers of grafting is accepted to be the BPh photolysis. In the work of Oster and Yang,[29] that first act of grafting initiation is assumed to be the splitting of a hydrogen atom off the polymer molecule. The mechanism suggested by Howard et al.[30] is widely acknowledged. In accordance with it, the BPh molecule is first excited to a triplet state. When that excited triplet interacts with a polymer matrix, a hydrogen atom splits off the polymer molecule and primary radicals, which initiate graft copolymerization, are formed:

$$(C_6H_5)_2CO \xrightarrow{h\nu} [(C_6H_5)_2CO]^* \rightarrow [(C_6H_5)_2CO]_T^* \quad (4)$$

$$[(C_6H_5)_2CO]_T^* + \text{polymer} \rightarrow (C_6H_5)_2\dot{C}-OH + \text{polymer}^{\cdot} \quad (5)$$

The polymer radicals thus formed initiate graft copolymerization and the diphenylhydroxymethane radicals induce homopolymerization that decreases E.

Figure 1 shows the ESP spectra of BPh (b, c) and of BPh adsorbed on PAN (a, d) in air (a, b) and in an argon (c, d) atmosphere. It is evident that small radical concentrations are registered when both pure BPh and BPh adsorbed on PAN are irradiated. At the same time, if PAN is irradiated under analogous conditions, radicals are not formed. That is the reason the established radical formation should be considered as a direct proof of the possibility of graft copolymerization onto PAN photosensitized by BPh radicals. The low radical concentration causes poor spectrum resolution and thus makes unclear the differences between the hyperfine structure of the spectra of the radicals formed during the irradiation of pure BPh or BPh adsorbed on PAN as well as the differences between the spectra of the radicals obtained in air and in an argon atmosphere. It is evident, however, that such differences exist and they are in agreement with the discussed mechanism of Howard et al.[30]

The kinetic behavior of radical generation is plotted on Figure 2. The initial rate of radical formation is considerably greater than that after 10–15 min of irradiation. The radical concentration achieved after 10 min irradiation of BPh adsorbed on PAN is 40% of the concentration of radicals formed after 2 h of irradiation. This makes possible the initiation of graft copolymerization by shorter (10–15 min) irradiation of the BPh adsorbed on PAN.

According to Iwakura and Takeda,[20] the increase in E of BPh-photosensitized graft copolymerization, when small quantities of copper and ferrous salts are added to the reaction feed, is a result of the catalytic oxidation of the diphenylhydroxymethane radicals to BPh, which results in a decreased possibility for homopolymer synthesis.

Within the framework of the discussed mechanism of Howard et al., the solvent influence over D and E can be related to its effect either on the process of BPh photoexcitation or on the quenching of the BPh triplet, or may be a result of the solvent interactions with the two kinds of primary radicals. The basic nitrogen atom is a prerequisite for more intensive participation of DMF in these interactions.

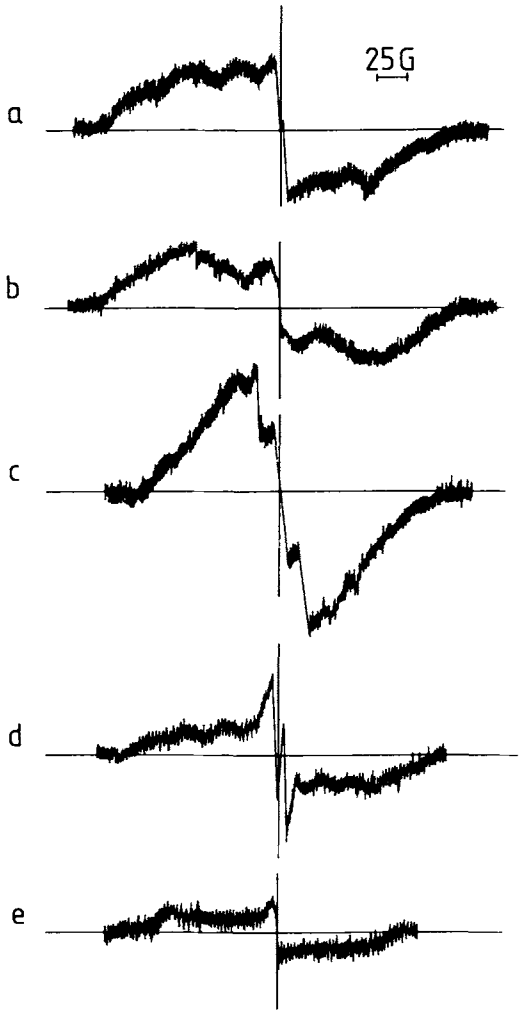

Figure 1 SPR spectrum obtained after photolysis (120 min) of BPh (b, c) and BPh adsorbed on PAN (a, d, e) either in air (a, b) or in an argon atmosphere (c, d, e). Spectrum e is obtained after the addition of GM to sample d. Scan range = 3.6 G/mm, field set = 3300 G, modulation amplitude = 5 G, modulation frequency = 10 dB, microwave frequency = 9.5 GHz, and room temperature = 22°C.

The great difference in the D, E, and C_{EG} values in experiments 1 and 2 (Table I) could be qualitatively explained in this way.

If the values of C_{EG} in experiments 1 and 3 (Table I) are compared, another interesting peculiarity can be noticed. The GM concentration in the polymerization feed of experiment 3 is decreased twofold compared to that of experiment 1, and the C_{EG} value is much more strongly reduced (10.6 times). A possible reason for this significant decrease in C_{EG} when GM and HEMA are cografted is the difference in the two monomer reactivities. In support of this assumption, experimental data on the compositions

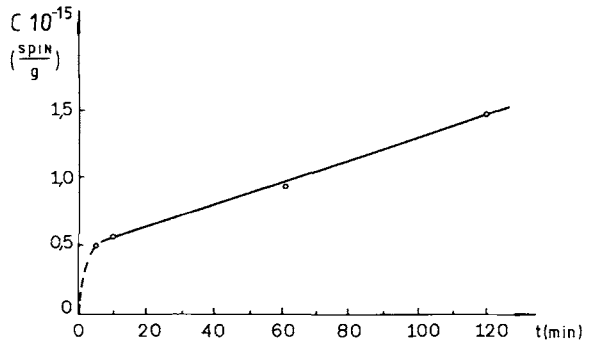

Figure 2 Kinetics of radical formation during the irradiation of BPh adsorbed on PAN at room temperature.

of copolymers, synthesized from reaction feeds with different comonomer concentration ratios, are presented in Table II. On the basis of these data, the reactivity ratios of the two comonomers are calculated by the Kelen–Tudos method[31] and are found to be $r_{GM} = 0.70 \pm 0.13$ and $r_{HEMA} = 2.74 \pm 0.14$. The reactivity ratios calculated by the Joshi–Joshi method[32] are $r_{GM} = 0.69 \pm 0.16$ and $r_{HEMA} = 2.72 \pm 0.15$. It should be noticed that these values characterize a heterogeneous copolymerization of GM and HEMA, as the synthesized copolymers have limited solubility in the water–MEK solvent mixture. This fact could explain the difference between the GM and HEMA reactivity ratios mentioned above and those, determined by ^{13}C-NMR spectra of the copolymers synthesized during a homogeneous copolymerization of GM and HEMA in DMF ($r_{GM} = 1.00 \pm 0.27$ and $r_{HEMA} = 0.74 \pm 0.29$).[33] Maybe this is one of the reasons for the existence of three quite different sets of values of GM and HEMA Q and e parameters: $Q_{GM} = 0.85$, $e_{GM} = 0.10$, $Q_{HEMA} = 0.80$, $e_{HEMA} = 0.20$[34]; $Q_{GM} = 0.96$, $e_{GM} = 0.20$,

Table II Dependence of the Mole Fraction of the GM Monomer Units (m_{GM}) in the GM–HEMA Copolymers on the Mole Fraction of the GM in the Initial Monomer Blend (M_{GM})

N	M_{GM}	m_{GM}	r_{GM}	r_{HEMA}
1	0.10	0.04		
2	0.20	0.09		
3	0.30	0.15	0.70 ± 0.15	2.73 ± 0.14
4	0.40	0.20		
5	0.50	0.33		
6	0.70	0.48		

The copolymerization was carried out in a solvent mixture consisting of MEK (84.6%) and water (7.7%); temperature 75°C; initiator AIBN (0.5%).

Q_{HEMA} = 1.78, e_{HEMA} = 0.39[35]; and Q_{GM} = 1.03, e_{GM} = 0.57, Q_{HEMA} = 0.80, and e_{HEMA} = 0.20.[36] The reactivity ratio values calculated on the basis of these parameters are r_{GM} = 1.07 and r_{HEMA} = 0.92 for the first set of Q and e values; r_{GM} = 0.48 and r_{HEMA} = 1.47, for the second one; and r_{GM} = 1.00 and r_{HEMA} = 0.84, for the third one. The experimental values of GM and HEMA reactivity ratios determined in this work are in close agreement with the theoretical values calculated using the second set of Q and e parameters.

The influence of the UV-source power on the graft copolymerization degree and efficiency has also been studied. The results presented in Table I were obtained when samples were irradiated with 125 W UV-light source. If all the experimental conditions are the same as in experiment 1 of Table I but the power of the UV source is 45 W, D and E equal 40.3 and 72.8%, respectively and C_{EG} = 2020 μmol/g. It is evident that the small decrease in these values is not in proportion to the decrease in the UV-source power.

Graft Copolymerization Kinetics

The knowledge of graft copolymerization kinetics can help control the D, E, and C_{EG} values. The kinetic curves in Figure 3 (C_{EG} vs. time) are relevant to the grafted copolymers synthesized in experiments 1 and 3 (Table I). It is important to note that both curves have an S-like shape and a sharp increase in the GM grafting velocity is observed 1.5–2 h after the beginning of the process. This copolymerization characteristic could be explained by the limited solubility of the growing chains mentioned above, the decreased mobility of the grafted propagating radicals, and a faster increase in the local viscosity near the PAN fibers than in the bulk. Because of these reasons, a local gel effect occurs near the PAN fibers at lower values of the total monomer concentration and conversion. The poly(GM) solubility in the water–MEK mixture is lower than that of the GM–HEMA copolymer. This results in a local gel effect appearing earlier if GM only is grafted onto PAN (curve 1 of Fig. 3). The gel effect can be observed most clearly when GM is grafted onto PAN in a solvent-free copolymerization feed. The graft copolymerization goes very quickly in this case (it ends within 5–10 min) and long-living propagating radicals captured by the gel net are indicated [Fig. 1(e)].

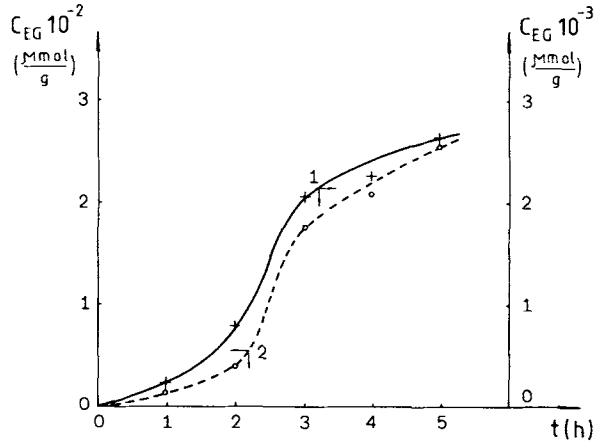

Figure 3 Kinetic dependencies of the concentration of epoxy groups (C_{EG}) in the copolymers synthesized by photoinitiated grafting of GM (curve 1) or of an equimolar mixture of GM and HEMA (curve 2) onto PAN at temperature of 75°C. Reaction feed composition: MEK (84.6%), water (7.7%), and comonomer mixture (7.7%).

The saturation of the kinetic curves after 3 h of copolymerization is caused by the monomer exhaustion. These dependencies show that the duration of the discussed graft copolymerization could be used as an effective regulator of C_{EG} and, hence, of D and E.

Characteristics of PA Immobilized onto the Grafted Copolymers

Figure 4 shows the dependence of the specific PA activity (A_{sp}) on the C_{EG} of the two immobilization matrices: grafted on PAN poly(GM) (curve 1) and grafted onto PAN copolymer of GM and HEMA (curve 2). The side chains consisting of HEMA and/or GM monomer units are synthesized under the conditions of experiments 1 and 3 (Table I), but the duration of grafting is varied. At low C_{EG}, a linear relationship is observed. This kind of dependence would be expected if the matrix surface is not yet densely occupied by enzyme molecules.[37] A deviation from linearity could be noticed at greater C_{EG}. This can be explained by the inability of a certain number of epoxy groups to interact with new enzyme molecules, as these groups are sterically inactivated by the previously bound macromolecules. When an enzyme monomolecular layer is formed on the matrix surface, the increase in C_{EG} does not cause any rise in A_{sp}.

The curves in Figure 4 differ considerably in the slopes of their first parts as well as in the A_{sp} limit value that is reached at great C_{EG}. It becomes clear that the differences are even greater if one considers that at equal D and E the C_{EG} of grafted GM–HEMA copolymer is of an order of magnitude lower than

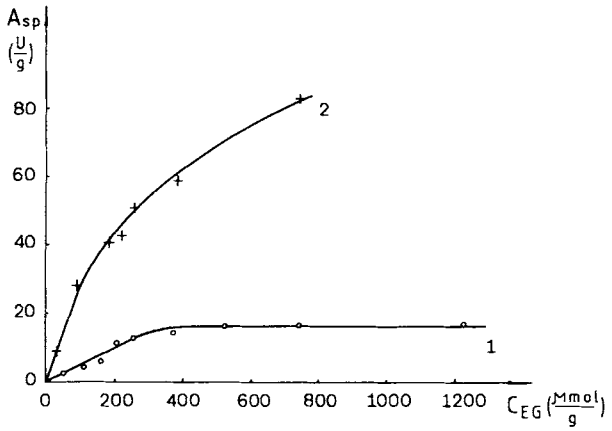

Figure 4 Epoxy group concentration dependence of the enzyme activity of penicillin–amidase immobilized on grafted onto PAN poly(GM) (curve 1) and copolymer of GM and HEMA (curve 2). The immobilization was done for 72 h in PA water solution (6000 U/g), pH = 7.5, and temperature 25°C.

that of the grafted poly(GM). Therefore, if C_{EG} of the two types of copolymers are the same, the amount of the grafted GM–HEMA copolymer is greater and provides a more hydrophilic carrier surface. This hydrophilicity ensures mild binding conditions and a lower degree of deactivation of the enzyme molecules. On the basis of the difference between the slopes of the first parts of curves 1 and 2 (Fig. 4), it can be estimated approximately that the degree of PA deactivation, when it is immobilized on a copolymer of GM and HEMA grafted onto

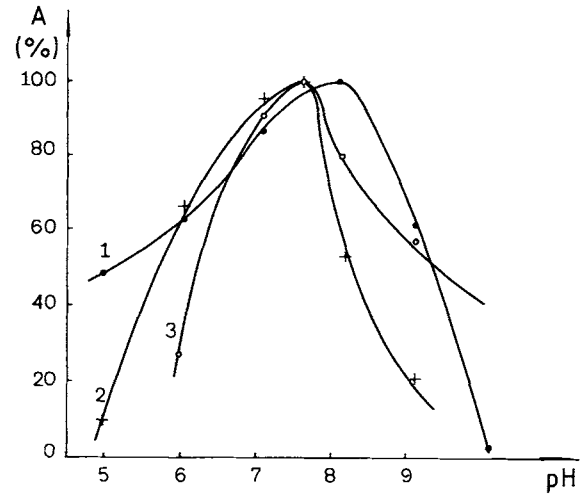

Figure 5 pH profiles of (1) native PA and PA immobilized on (2) GM and a (3) GM–HEMA copolymer grafted onto PAN. Temperature: 40°C. The enzyme activity A is presented in percentage of its value in pH_{opt}.

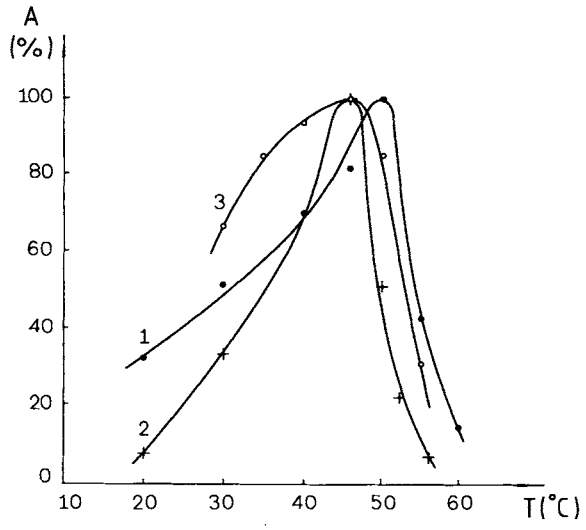

Figure 6 Temperature profiles of (1) native PA and PA immobilized on (2) GM and a (3) GM–HEMA copolymer grafted onto PAN. pH_{opt} = 8.0. The enzyme activity A is presented in percentage of its value in T_{opt}.

PAN, is five times lower than if the matrix is a copolymer with the same C_{EG} but with side chains of poly(GM). So, it is evident that the copolymer of GM and HEMA grafted on PAN is more suitable for PA immobilization than is the matrix that represents the poly(GM) copolymer grafted onto PAN.

The great difference in the dependence of A_{sp} on C_{EG} of the two carriers raises the expectation that the optimum pH and temperature for PA immobilized on them will also differ considerably. Contrary to expectations, pH_{opt} = 7.5 and T_{opt} = 45°C are the same for PA immobilized on both copolymers (Figs. 5 and 6). The characteristics for native PA are pH_{opt} = 8.0 and T_{opt} = 50°C. The identity of pH_{opt} and T_{opt} for the two carriers as well as their deviation from these values for the native enzyme could be a result of interactions between the immobilized enzyme macromolecules after the formation of a dense layer on the matrix surface. That is the reason for the negligible influence of the carrier surface.

CONCLUSIONS

1. Graft copolymerization of hydroxyethyl methacrylate (HEMA) and/or glycidyl methacrylate (GM) on PAN photosensitized by benzophenone (BPh) proceeds in a MEK–water solvent mixture. Copolymers with an adequate degree and efficiency of grafting are obtained. The addition of DMF to the solvents is undesirable.

2. Self-acceleration of the HEMA and GM graft copolymerization onto polyacrylonitrile (PAN), at low total monomer concentration and conversion, is established.
3. During the grafting of HEMA and GM on PAN, the side chains of the synthesized copolymers are enriched in HEMA units because of the greater reactivity of this comonomer. As a result of this, the degree of deactivation of penicillin–amidase on this matrix is five times lower than that of penicillin–amidase immobilized by poly(GM) grafted onto PAN.
4. The optimum pH and temperature values of penicillin–amidase immobilized by poly(GA) or HEMA–GA copolymer grafted onto PAN are shifted to lower values (0.5 pH-units and 5°C) than those of the native enzyme.

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