Kinetic Study of Acrylic Monomer Grafting in the Presence of a Polyfunctional Monomer onto Radioperoxided Poly(Ethylene–Tetrafluoroethylene) Copolymer

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SYNOPSIS

Acrylic acid (AA), methacrylic acid (MA) and diethyleneglycol dimethacrylate (DEGDM) are grafted onto 100 μm radioperoxided poly(ethylene–tetrafluoroethylene) copolymer (ETFE). The influences of the homopolymerization inhibitor, the solvent, the grafting temperature, and the monomer content on the grafting kinetics are studied. For the grafting of acrylic monomers, the limitation of the grafting yield is more important for AA grafting whatever the nature of the metallic salt; the difference between the two homopolymerization inhibitors is their respective concentration to obtain a given grafting yield. For the AA + DEGDM cografting, the grafting yield increases with the DEGDM content of the grafting solution. In both cases, the overall activation energy has been calculated, and its variation as a function of the composition of the grafting solution is discussed. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Numerous methods have been used to prepare grafted polymers last years, including both conventional chemical and radiochemical methods. The advantages of radiochemical methods are an ease of preparation as compared to chemical methods, a general applicability to a wide range of polymer combination, and a possible grafting both on the surface and in the polymer matrix. Acrylic acid (AA) grafting has widely been studied as well on olefinic polymer[1–8] as well as on fluorinated matrix.[9–11] Metallic salts are used to limit both the monomer homopolymerization and the grafting yield. However, physicochemical characterizations have pointed out the nonstability of such films immersed in basic solutions.[10]

Garnett and coworkers[12,13] have shown that the presence of polyfunctional monomers such as divinyl benzene and trimethylolpropane triacrylate as additives enhanced significantly the grafting yield at certain monomer concentrations during the copolymerization of styrene onto polyethylene films. In the same way, the addition of diethylene glycol–dimethacrylate (DEGDM) enhanced the grafting yield of acrylic acid onto polyethylene films.[14]

Although numerous studies have been published about AA grafting onto polyethylene films, there have been only a few papers about AA grafting onto fluorinated polymers, and, to our knowledge, no work has been undertaken about AA + DEGDM cografting onto fluorinated polymers.

The aim of this work is to study the influence of the nature of metallic salts and of the presence a difunctional crosslinking agent, DEGDM, on the kinetic grafting of acrylic acid. The study is achieved on poly(ethylene-tetrafluoroethylene) copolymer (ETFE).

EXPERIMENTAL

Materials

Poly(ethylene–tetrafluoroethylene) copolymer (ETFE) of 100 μm thickness (Hostaflon ET from Hoechst Co.) was used as trunk polymer. Acrylic acid (AA) and methacrylic acid (MA) from Prolabo

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Chemical Co. and diethylene glycol–dimethacrylate from Rhom Chemicals Co. were used as reagents. Mohr's salt and copper sulfate from Flucka Chemicals Co. were used as homopolymerization inhibitors.

Grafting

ETFE films were prealably irradiated in air by electron beams of an accelerator (Radiation Dynamics Inc.) under a 1.5-MeV beam and a 10-mA current. The preirradiated films (3 × 4 cm) were introduced in a glass reactor containing a solution composed of acrylic acid (AA), methacrylic acid (MA), diethylene glycol–dimethacrylate (DEGDM), of homopolymerization inhibitors (Mohr's salt or copper sulfate), and solvents (methanol and water). After being deaerated by nitrogen bubbling, the glass reactor was immersed in a thermostat during grafting time. Then, grafted films were taken out from the grafting solution and washed with water and methanol. After drying under vacuum under a temperature of 45°C, they were weighed and the degree of grafting or grafting yield (G_Y) was calculated according to the following relation:

$$G_Y = \frac{m - m_0}{m_0}$$

where m and m_0 are the weight of the grafted film and initial film, respectively.

Exchange Capacity

The principle has been described elsewhere.[15] Its measurement allows determination of the proportion of the AA or MA monomer grafted onto the polymer film, DEGDM having no exchanging groups.

RESULTS AND DISCUSSION

Acrylic Acid and Methacrylic Acid Graftings

Influence of the Grafting Solvent

The grafting solvent has to be:

—a good solvent for the monomers and the different additives
—a good swelling agent of the graft polymer

in order to favor diffusion of the monomer through the polymer matrix and to allow the accessibility of peroxidic sites located deeply in the film.

Eventually, it can play a role of chain transfer agent of the growing polymeric radicals. This reaction is mainly observed in the case of a solvent having a high transfer constant.

For the AA grafting, water and methanol were used. The variation of the grafting yield as a function of the solvent proportion in the grafting solution is illustrated in Figure 1. The increase of the grafting yield with the water content of the grafting solution is probably due to a facilitated diffusion of the monomer through the macromolecular network of the grafted ETFE film. Water is the best swelling agent of the polyAA.

In the same way, under identical experimental conditions, the grafting yield is lowered if butanol is substituted for methanol. Comparing the influence of water, methanol, and butanol, it appears that the enhancement of AA grafting is related to the solvent polarity.

Influence of the Homopolymerization Inhibitor

In the preirradiation method, monomer can homopolymerize by the active sites formed by chain

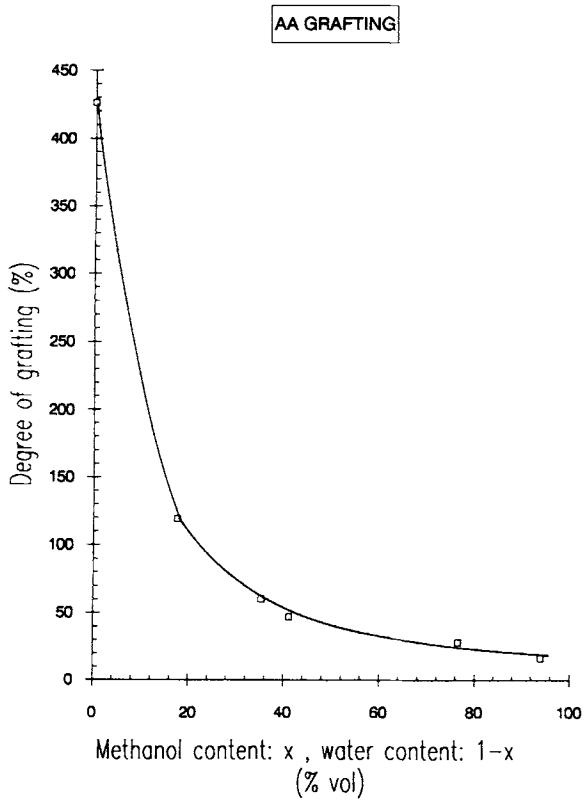

Figure 1 Influence of solvent on acrylic acid grafting. Grafting solution: AA 22 vol %; solvent 78 vol %; copper sulfate 1.7×10^{-4} g/L. Grafting temperature 65°C; graft ing time 20 h.

transfer reaction of growing polymer radical and/or by dissociation of peroxides. Under an air atmosphere, the irradiation of polyethylene and polytetrafluoroethylene, on the one hand, and polypropylene, on the other, leads essentially to formation of diperoxides and hydroperoxides, respectively.[16] Consequently, the homopolymer formed in the grafting solution should have its origin in the decomposition of either the hydroperoxide or the diperoxide POOR, during the AA grafting onto ETFE film. P is the polymeric radical and R is a lateral chain having a low molecular weight.

The presence of metallic salts reduces considerably the monomer homopolymerization. It is well known that the most efficient components for inhibiting AA and MA homopolymerization are the copper and iron salts. The influence of Mohr's salt and copper sulfate have been studied.

Another effect of the metallic cations is to limit the grafting yield as can be seen, for the metallic salts studied, in Figure 2. The difference between the two homopolymerization inhibitors is their respective concentrations to obtain a given grafting yield. This concentration is 100 times lower for the copper sulfate as reported in Table I.

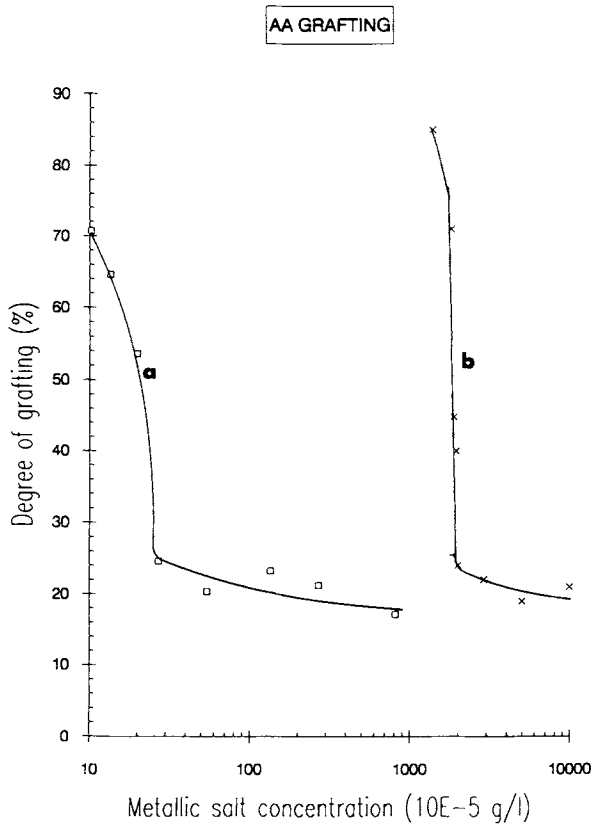

Figure 2 Influence of metallic salt on acrylic acid grafting: (a) copper sulfate; (b) Mohr's salt. Grafting solution: AA 22 vol %; solvent 78 vol %; grafting temperature 65°C. Grafting time 20 h.

Table I Concentration of Homopolymerization Inhibitor vs. Grafting Yield[a]

Grafting Yield	Homopolymerization Inhibitor	
	Copper Sulfate	Mohr's Salt
85%	1.55×10^{-4} g/L (6.2×10^{-7} mol/L)	1.8×10^{-2} g/L (4.6×10^{-5} mol/L)
40%	1.7×10^{-4} g/L (6.4×10^{-7} mol/L)	1.9×10^{-2} g/L (5×10^{-5} mol/L)

[a] AA 22 mol %; methanol 50 vol %, water 28 vol %; grafting temperature 65°C; grafting time 20 h; dose 6 Mrads.

The influence of metallic salt depends on the nature of the grafted monomer. Under the same experimental conditions, if we compare the reactivity of AA and MA, the limitation of the grafting yield is more important for AA grafting whatever the nature of the metallic salt. For example, for a concentration of copper sulfate equal to 10^{-2} g/L, the AA grafting yield is close to 20% while that of MA reaches 80–90%. An increase of the copper sulfate concentration has no influence on the MA grafting yield. The only observed phenomenon is the more important coloring of the film due to the fixation of copper cations on the carboxylic sites of the grafted MA.

The difference between the AA and the MA reactivities can be explained as follows:

—The metallic salts are more soluble in the grafted polyAA than in the grafted polyMA, limiting in this way the grafting by a process of chain transfer reaction.
—The diffusion of metallic species through the different grafted layers is weaker in the case of MA grafting.

The grafting process is a reaction controlled mainly by the diffusion of species of the grafting solution (monomers and metallic salts). The mechanism of grafting can be decomposed as follows.

(i) Peroxide decomposition:

$$\begin{matrix}\text{POOP} \\ \text{or} \\ \text{POOR}\end{matrix} \xrightarrow[k_1]{\text{temperature}} 3\ \text{PO}\cdot + \text{RO}\cdot$$

This decomposition leads to the formation of both PO• radicals, which will be able to start grafting,

and RO$^{\cdot}$ radicals, which will be able to start the monomer homopolymerization (R is either an hydrogen atom or a ETFE having a low molecular weight).

(ii) Grafting initiation:

$$PO\cdot + M \xrightarrow{k_2} POM\cdot$$

$$PO\cdot + In \xrightarrow{k_3} \text{deactivated polymer radical}$$

(iii) Homopolymerization initiation:

$$RO\cdot + M \xrightarrow{k_4} ROM\cdot$$

$$RO\cdot + In \xrightarrow{k_5} \text{deactivated polymer radical}$$

(iv) Propagation:

$$POM_{(n-1)}\cdot + M \xrightarrow{k_6} POM_n\cdot$$

$$ROM_{(n-1)}\cdot + M \xrightarrow{k_7} ROM_n\cdot$$

(v) Termination:

$$POM_n\cdot + In \xrightarrow{k_8} \text{deactivated grafted polymer}$$

$$ROM_n\cdot + In \xrightarrow{k_9} \text{deactivated homopolymer}$$

Here the k_i (i = 1–9) are the rate constants, "In" is the homopolymerization inhibitor, and M is the monomer.

The previous mechanism presents only the competitive reactions between the monomer and the homopolymerization inhibitor in order to explain the experimental results. Indeed, the grafting mechanism is more complicated due to the different reactions such as transfer and combination. These reactions occur inevitably between the numerous components of the grafting solution (film, monomers, solvents).

The absence of the homopolymer in the solution coupled with the grafting polymerization of the monomer on the film is explained generally by a more important monomer diffusion than that of metallic cation through the matrix polymer i.e.,

$$\frac{k_5}{k_4} \gg \frac{k_3}{k_2}$$

In the same way, the difference in the efficiency of the two metallic salts can be explained by a more important diffusion of Fe^{2+} than Cu^{2+} through the grafted polymer matrix, i.e.,

$$\left(\frac{k_8}{k_6}\right)_{Fe^{2+}} \gg \left(\frac{k_8}{k_6}\right)_{Cu^{2+}} \quad \text{for the same monomer}$$

The difference in the monomer reactivities can be explained as previously:

$$\left(\frac{k_8}{k_6}\right)_{AA} \gg \left(\frac{k_8}{k_6}\right)_{MA} \quad \text{for the same metallic salt.}$$

Influence of Grafting Temperature

The variation of the AA grafting yield versus time for different temperatures is illustrated in Figure 3 in the case where Mohr's salt acts as homopolymerization inhibitor. An increase of temperature is followed by an increase of the grafting rate. The grafting yield exhibits a maximum value, for a temperature of 45°C, after a 20-h reaction time. The same effects are observed in the presence of copper sulfate.

The temperature effect on grafting characteristics is difficult to analyze. An increase favors both the peroxide decomposition and the monomer diffusion rate through the polymer matrix. These two effects lead to an increase of the grafting rate (initiation and propagation). However, the decrease of viscosity

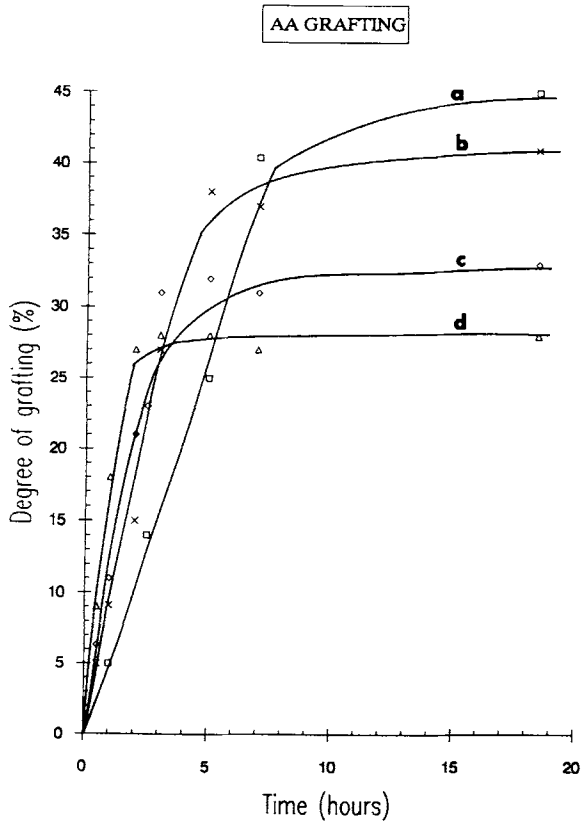

Figure 3 Kinetics of acrylic acid grafting. Influence of temperature (°C): (a) 45; (b) 55; (c) 65; (d) 75.

of the grafting solution due to the temperature increase leads to an enhancement of the mobility of macromolecular chains and therefore favors their recombination. By this way, the formation of short grafted chains will be favored by high temperatures.

From the initial grafting rates, the overall activation energy of the grafting reaction can be calculated using the Arrhenius relation. In the case of AA grafting, the plots of the logarithm of the initial grafting rate versus the inverse of the temperature lead to overall activation energies of 33 and 35 kJ mol^{-1} in the presence of copper sulfate and Mohr's salt, respectively.

As a conclusion of the AA and MA grafting onto ETFE films, the nature of the homopolymerization inhibitor does not play a main role in the grafting reaction. The only difference is the initial inhibitor concentration necessary to obtain a given grafting yield. This difference is related both to the variation of the diffusion rate of the metallic species through the polymer matrix and to the difference of the solubilities of the metallic cations in the grafted polyAA and polyMA.

AA + DEGDM Cografting

For the different experiments, three monomer compositions of the grafting solution have been studied (AA vol %/DEGDM vol %): 18 20/2; 4; 16/6. The amount of the monomers represents 22 vol % of the grafting solution.

Although sulfuric acid is necessary to graft AA alone or with DEGDM (for lower DEGDM content) onto polyethylene,[14] this acid is not required for ETFE, whatever the proportion of these two monomers in the grafting solution.

Influence of the AA and DEGDM Content

The influence of the monomer content on the grafting yield is illustrated in Table II. The grafting yield increases with the DEGDM content in the grafting

Table II Influence of the Monomer Content of the Grafting Solution on the Grafting Yield[a]

Monomer Composition (% AA/% DEGDM)	16/6	18/4	20/2
Grafting yield (%)	103	83	73
AA grafting yield (%)	32	33	43
DEGDM grafting yield (%)	71	50	30

[a] Monomers 22 vol %; methanol 50 vol %; water 28 vol %; copper sulfate 10^{-4} g/L; grafting temperature 65°C; grafting time 20 h; dose 6 Mrads.

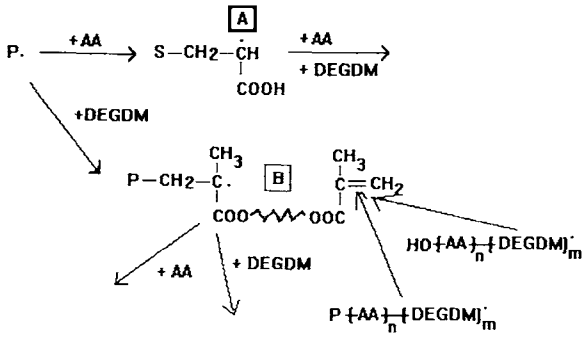

Figure 4 Part of grafting mechanism of AA + DEGDM onto ETFE (P represents a polymer radical produced during peroxide decomposition).

solution. Exchange capacity measurements allow the determination of the AA and DEGDM contents onto the grafted film. Results shown that AA content is practically constant.

According to Figure 4, when DEGDM is grafted, the B component presents a double reactivity due to:

(i) The radical function on which the polymerization will go on with the fixation of either an AA or a DEGDM molecule. This fixation depends on the monomer content in the grafting solution.
(ii) The double bond which can react with either the homopolymer forming a new grafted chain, or a growing polymer chain leading to a secondary crosslinking.

The difference of the monomer reactivities onto a 100 μm thickness ETFE film versus the two monomers content is not important compared to the results obtained onto a 25-μm-thick polyethylene film,[14] where the grafting yield is multiplicated by 30 when the composition varies from 20 vol % AA/2 vol % DEGDM to 16 vol % AA/6 vol % DEGDM. Both the grafting rate and the final grafting yield depend not only on the polymerization rate of the two monomers but also on the diffusion rate.

DEGDM is generally used as elastomer crosslinking. PolyDEGDM is not swollen by the solvents involved for the AA grafting (water and methanol). It is therefore difficult to graft DEGDM alone, and the obtained yields never exceed 10% onto ETFE. This grafting is only obtained on the ETFE surface. As this surface does not swell in the grafting solution, DEGDM cannot reach peroxide sites located more deeply within the film. Therefore, the diffusion of the two monomers through the polymer matrix

is only due to the AA grafting, which can explain the difference in the observed reactivities onto a 25- and a 100-μm-thick film. In the first case, due to the weak thickness of the film, the grafting rate is mainly controlled by the polymerization rate while, in the second case, the diffusion process has to be taken into account.

Influence of the Nature of the Homopolymerization Inhibitor

The variation of the grafting yield vs. concentration of copper sulfate or Mohr's salt is illustrated in Figures 5 and 6 for different monomer concentrations in the grafting solution. For a same concentration, the grafting increases with the DEGDM content in the grafting solution whatever is the nature of the inhibitor. As DEGDM favors the grafting propagation, the amount of the inhibitor necessary for limiting the grafting increases with the DEGDM content.

Influence of the Grafting Temperature

As we have seen previously, the nature of the homopolymerization inhibitor and of the monomer composition of the grafting solution modifies both the grafting rate and the final grafting yield. In order to determine the overall activation energy of the reaction, the influence of the temperature on the grafting kinetics has been studied. The composition of the five grafting solutions differs on the nature of homopolymerization inhibitor (copper sulfate or Mohr's salt) and on the monomer composition (AA/DEGDM (vol %/vol %): 20/2; 18/4; 16/6). Figures 7 and 8 represent the grafting kinetics versus temperature for a same composition of the grafting solution but for two different homopolymerization inhibitors. These plots present the same variations as that for the AA grafting. Whatever the nature of the inhibitor and the monomer composition of the grafting solution, an increase of the temperature leads to an increase of the grafting rate. However, the temperature for which the maximum value of the grafting yield is reached depends on the monomer composition of the grafting solution. This temperature increases with the DEGDM content. In the same way, an increase of the temperature decreases the solution viscosity, favoring the monomer diffu-

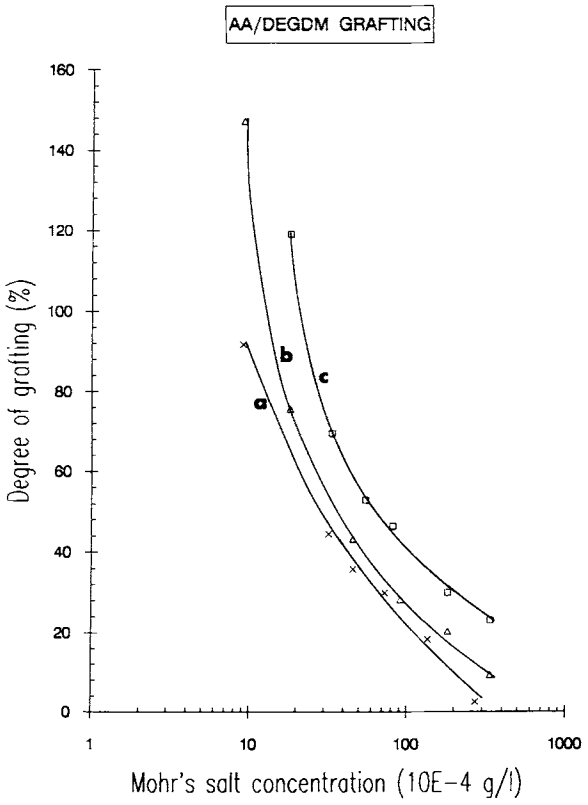

Figure 5 Influence of Mohr's salt concentration on AA + DEGDM cografting. Composition (AA vol %/DEGDM vol %): (a) 20/2; (b) 18/4; (c) 16/6.

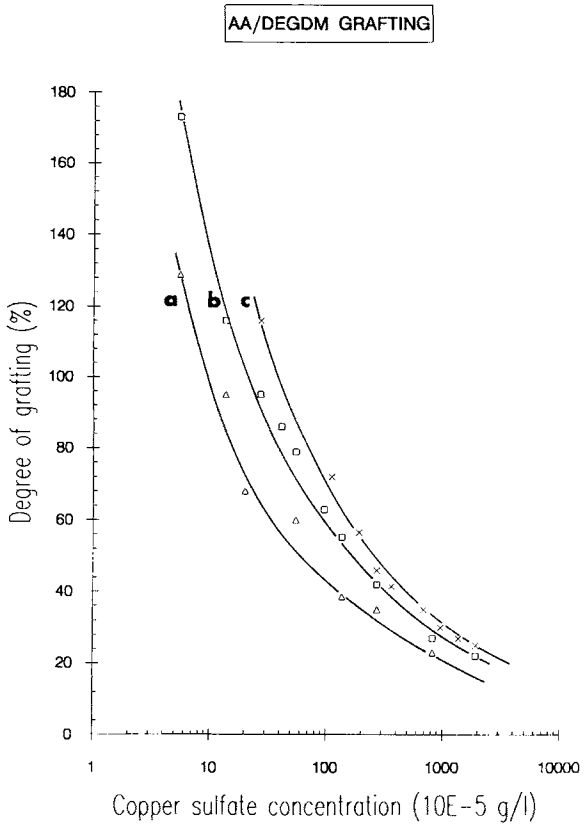

Figure 6 Influence of copper sulfate concentration on AA + DEGDM cografting. Composition (AA vol %/DEGDM vol %): (a) 20/2; (b) 18/4; (c) 16/6.

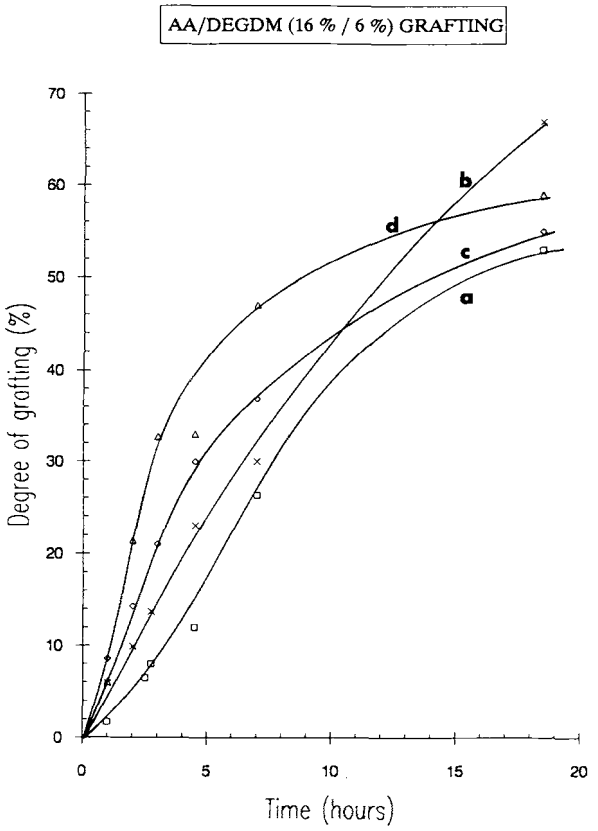

Figure 7 Kinetics of AA + DEGDM cografting. Influence of temperature (°C): (a) 45; (b) 55; (c) 65; (d) 75. Composition: AA 16 vol %; DEGDM 6 vol %. Homopolymerization inhibitor: copper sulfate.

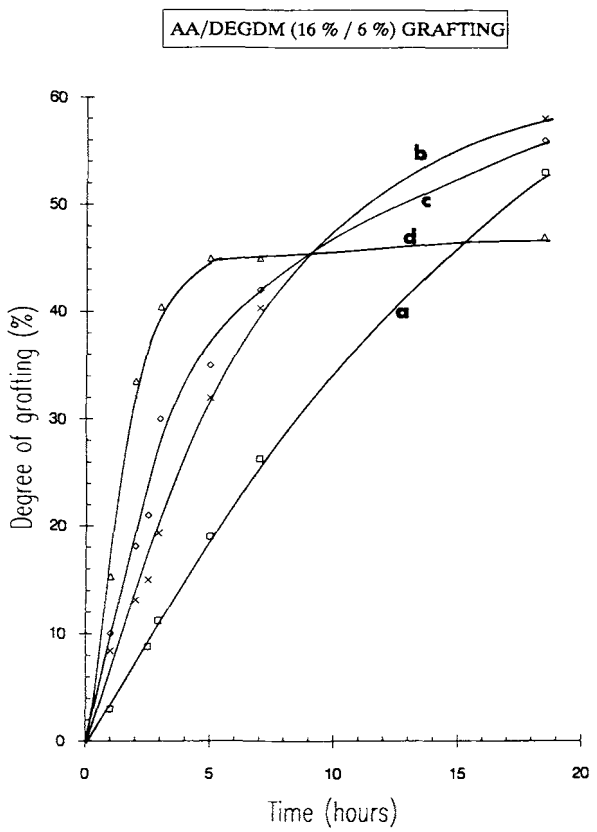

Figure 8 Kinetics of AA + DEGDM cografting. Influence of temperature (°C): (a) 45; (b) 55; (c) 65; (d) 75. Composition: AA = 16 vol %; DEGDM = 6 vol %. Homopolymerization inhibitor: Mohr's salt.

sion and therefore the grafting propagation more deeply in the polymer matrix. The values of the overall activation energies are reported in Table III. In order to explain the variation of these values, we have to take into account the following observations:

(i) Mohr's salt catalyses DEGDM grafting.[14] Without this salt and even with other metallic salts such as ferrous sulfate, copper sulfate, and ammonium sulfate, no grafting occurs. At this time, no logic explanation can be given about the effect of Mohr's salt.

(ii) The overall activation energy E_a can be decomposed into five terms[16]:

$$E_a = E_i + E_p + E_t + E_\eta + E_d$$

where E_i, E_p, E_t, E_η, and E_d are the partial activation energies of initiation, propagation, termination, viscosity, and diffusion, respectively.

(ii-a) The initiation activation energy E_i will depend on the nature of the homopolymerization inhibitor. As a matter of fact, in the presence of Mohr's salt, the grafting is begun by the fixation of AA or of DEGDM molecules while, in the presence of copper sulfate, grafting is begun only by the fixation of a AA molecule. Therefore, E_i

Table III Overall Activation Energies of Grafting Reaction vs. the Monomer Content and the Nature of the Homopolymerization Inhibitor

Monomer Composition (% AA/% DEGDM)	Mohr's Salt	Copper Sulfate
22/0	35 kJ mol^{-1}	33 kJ mol^{-1}
20/2	20 kJ mol^{-1}	27 kJ mol^{-1}
18/4	—	36 kJ mol^{-1}
16/6	49 kJ mol^{-1}	44 kJ mol^{-1}

will be lowered in the presence of Mohr's salt as well as of copper sulfate.

(ii-b) The propagation activation energy E_p depends on the monomer proportion in the grafting solution. An increase of DEGDM content will favor the homopolymerization of the two monomers, leading to a decrease of E_p.

(ii-c) The viscosity activation energy E_η can be neglected, taking into account the weak concentration and the good solubility of these monomers in the water/methanol solution. E_η will be weakly influenced by both the nature of the homopolymerization inhibitor and the monomer proportion of the grafting solution.

(ii-d) The diffusion activation energy E_d will be favored by a weak content of DEGDM because the diffusion process is controlled only by the swelling of the polymer matrix which is directly related to the AA content.

The variation of the overall activation energy E_a will depend on both the influence of the composition of the grafting solution and the nature of homopolymerization inhibitor on the different partial activation energies. Some effects act contrarily; for example, an increase of the DEGDM content favors the propagation process but disadvantages the diffusion process.

This last observation may explain the variation of E_a with the DEGDM content of the grafting solution (Table III). With Mohr's salt as well as with copper sulfate, the initial decrease is followed by a progressive increase of E_a, when the DEGDM content increases in the grafting solution. Moreover, the value of E_a for the composition (AA = 16 vol %, DEGDM = 6 vol %) is higher than that for a solution without DEGDM.

In this way, the higher value of E_a for the composition (20 vol %, 2 vol %) in the presence of copper sulfate with respect to Mohr's salt can be explained by the influence of Mohr's salt on the beginning of the DEGDM grafting reaction.

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