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SYNTHESIS, CHARACTERIZATION, AND POLYMERIZATION OF NEW METHACRYLATE ESTERS HAVING PENDANT AMIDE MOIETIES

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ABSTRACT

In this paper, the synthesis of a number of new methacrylate esters containing amide group are described. The monomers produced from the reaction of corresponding α-chloro-N-aryl or -N-alkyl acetamides with sodium methacrylate were polymerized with AIBN as initiator. The monomers and their polymers were characterized by IR, ^{1}H- and ^{13}C-NMR spectroscopy. The glass transition temperature and thermal decomposition temperature of the polymers were investigated by DSC-50 and TGA-50 thermobalance, respectively. The photocrosslinking properties of the polymers were also discussed.

Key Words: α-Chloro-N-aryl or -N-alkyl acetamide; Thermal decomposition temperature; Methacrylate esters; Photocrosslinking properties

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INTRODUCTION

Nowadays there exists a strong demand for "functional polymers" with very specific properties. In polymer science, the improvement of the mechanical properties has been the center of interest for many years, but today special electrical and optical properties of polymers receive an increasing interest. Functional groups give the polymer structure special character, substantially different from the inherent properties of the basic polymer chain.[1] In recent years, some comprehensive work has been published on functional monomers and their polymers.[2–4] Increasing interest in the development of speciality polymers (functional polymers, polymer supports) in recent years has led to a rich arsenal of methodologies and procedures for the laboratory synthesis of functional monomers. Within the last few years, we have synthesized a number of such "functional polymers" in our group at the University of Firat. These include substituted polyphenacylmethacrylates with photochemical properties [5–7] and new polyarylhydroxyethyl methacrylate containing cyclobutane ring.[8,9]

Acrylate and methacrylate polymers have figured prominently in the development of soft tissue compatible materials,[10] and orthopedic [11] and dental cements.[12] Acrylate- and methacrylate-activated vinyl esters are readily polymerized by free radical polymerization (FRP) to form linear, branched, or network polymers.[13]

The effect of polymer structure on the reactivity and properties of reactive moieties is very important for the chemical modifications and for the eventual applications of reactive polymers.[14,15] Functionalized polymers have wide applications for various biological and technological purposes.[16,17] Many polymers with reactive functional groups are now being synthesized, tested, and used, not only for their macromolecular properties but also for the properties of the functional group. These groups provide an approach to a subsequent modification of the polymer for specific end applications.[18]

Fridkin et al. [19] introduced the polymeric reagent method for peptide synthesis that made use of an insoluble polymer-supported amino and active ester as the carboxyl component for coupling with the soluble amino component polymeric benzoic anhydrides that have been used for benzoylate alcohols and amines,[20] and N-trifluoroacetyl nylons that have been employed for the trifluoroacetylation of alcohols and amines.[21]

As far as we know, no reports have been observed in the literature about the synthesis, polymerizations, and use of methacrylate esters having pendant amide moieties.

We report here the preparation of new methacrylate esters containing an amide group. The keto group was introduced into the amine by a Schotten-Baumann reaction with acyl halide using K_2CO_3 catalyst. In the present study, the acyl halides used were $ClCOCH_2Cl$ (chloracetylchloride).

This article will focus on a novel synthetic method for the preparation of a wide variety of methacrylate esters with various side groups. In the first part of this paper, the synthetic approach, the acylation of different amines with reactive acyl chloride group, will be introduced and some general aspects of amine analogous reactions are discussed. Afterward, the synthesis of the reactive prepolymers is described in more detail, followed by a number of examples for the preparation of polymethacrylate esters with simple polymers that we used in model studies and go step to step to more complex architectures with more than one functional group. The latter are of interest in the field of different amide group polymers. Since one aim of this article is to demonstrate the case of the synthetic procedure and the wide variety of functional groups that can be attached to polymer backbone, some representative experimental procedure are included for future studies.

EXPERIMENTAL

Materials

Benzylamine, aniline, 4-nitroaniline, 4-aminobenzaldehyde, and chloroacetylchloride (Merck) were used as received. Sodium methacrylate, 1,4-dioxane, potassium carbonate, acetonitrile, sodium iodide, and anhydrous magnesium sulphate (Aldrich) were used as received. 2,2′-azobisisobutyronitrile was recrystallized from chloroform-methanol. Triethylbenzylamoniumchloride (TEBAC) was prepared by reacting triethylbenzylamine (1 mol) with amoniumchloride (2 mol). All the other chemicals were analytical grade commercial products. They were used without any further purification.

Characterization Techniques

IR spectra were measured on a Mattson 1000 FT-IR spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl^3$ with tetramethylsilane as the internal standard using a Jeol FX 90 Q 90 MHz spectrometer. Thermal data were obtained by using a Shimadzu DSC-50 instrument and TGA-50 thermobalance in N_2 atmosphere. A 500-W high-pressure mercury lamp was used in UV stability studies.

Typical Procedure for the Reaction of Amine with Chloroacetylchloride Using K_2CO_3 (1)

A typical procedure for the acylation reaction of amine with chloracetylchloride was as follows: Amine (1 mol) and K_2CO_3 were dissolved in 20 mL of anhydrous benzene at 0°C, and then 1.1 mol of chloracetylchloride was added dropwise to the solution. The reaction mixture was stirred at room temperature for 15 hours. The organic layer was washed several times with diethylether and dried over $MgSO_4$. After removing diethyl ether, α-chlor-N-aryl or -N-alkyl acetamide was crystallized from methanol. Yield: 75%.

Typical Procedure for the Reaction of α-Chloro-N-aryl or -N-alkyl Acetamide with Sodium Methacrylate Using TEBAC (Monomer Synthesis) (2)

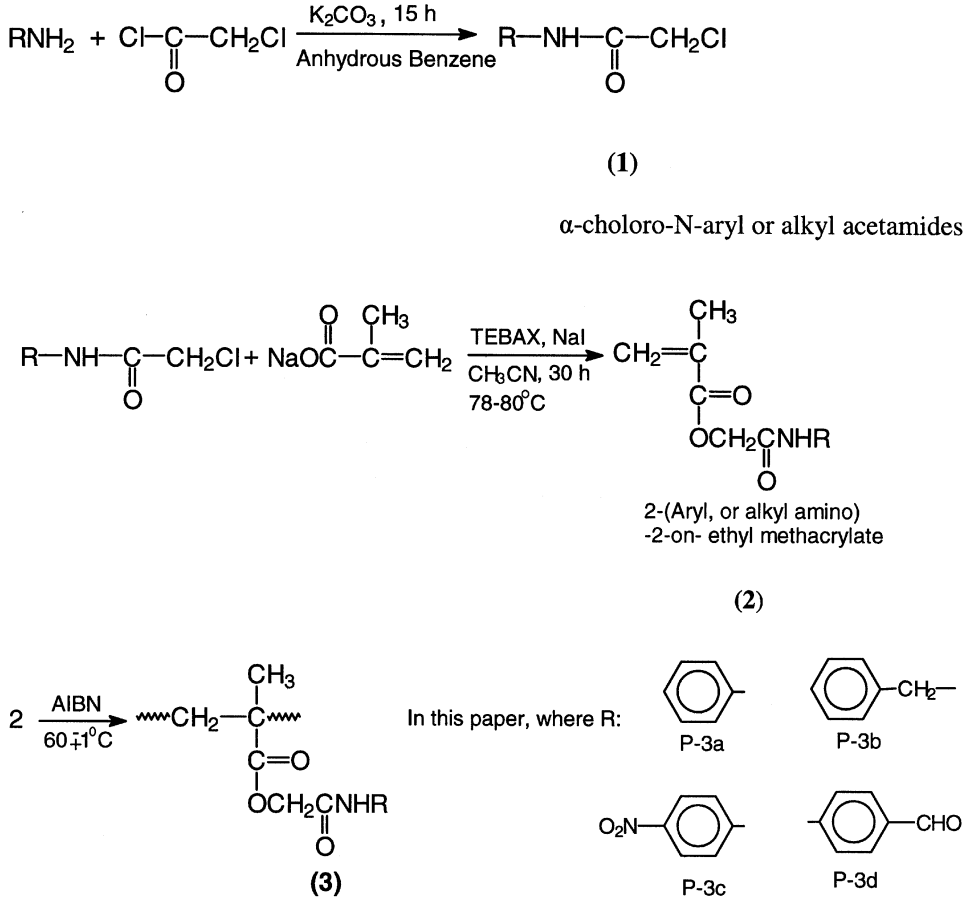
1 mol α-chloro-N-aryl or,-N-alkyl acetamide, 1.1 mol sodium methacrylate, 0.1 mol TEBAC, and 0.1 mol NaI as catalyst were stirred in 50 mL acetonitrile at 75–80°C in a reflux condenser for 30 hours in the presence of 100 ppm hydroquinone as the inhibitor. Then the solution was cooled to room temperature and neutralized with a 5% KOH solution. The organic layer was washed several times with water, and the water layer was washed with diethyl ether a few times. The acetonitrile layer and diethyl ether layer were collected and dried over anhydrous $MgSO_4$ overnight. Acetonitrile and diethyl ether were evaporated. The organic layers were collected and the residue was distilled at 128°C at 5 mm Hg to give a colorless liquid. Yield: 70%.

Polymerization of (2)

2 was freed from inhibitor by washing with a dilute KOH solution followed by distilled water and then drying over anhydrous $MgSO_4$. Appropriate amounts of 2 and 1,4-dioxane and 2,2′-azobisisobutyronitrile (2% of the weight of the monomer) were placed in a reaction tube and purged with argon for 10 minutes. The sealed tube was kept at 60 ± 1°C for 48 hours. The reaction contents were poured dropwise into a large excess of n-hexane. The polymer was purified by reprecipitation with n-hexane from a 1,4-dioxane solution and finally dried under vacuum (conversion 75%).

RESULTS AND DISCUSSION

As shown in Sch. 1, we propose a new route for methacrylate esters having pendant amide moieties. The yields of the reactions in Sch. 1 are of medium quantity (70–80%).



Scheme 1.

The esterification of sodium methacrylate with various α-chloro-N-aryl, or alkyl acetamides were also examined using TEBAX under the same conditions. The FT-IR spectra of the monomers m-3b and m-3c is shown in Fig. 1. The ^{1}H-NMR spectra of the monomers m-3c and m-3d is shown in Fig. 2.

Structure Characterization of the Polymers

In the IR spectrum of the polymers, P-3b showed some characteristic absorption peaks at 3340 cm^{-1}, characteristic of a NH stretching vibration for secondary amide (bonded NH), a narrow band at 1640 cm^{-1} (amide 1) ascribed to a C=O stretching vibration, and the amide II band at 1525 cm^{-1} for the

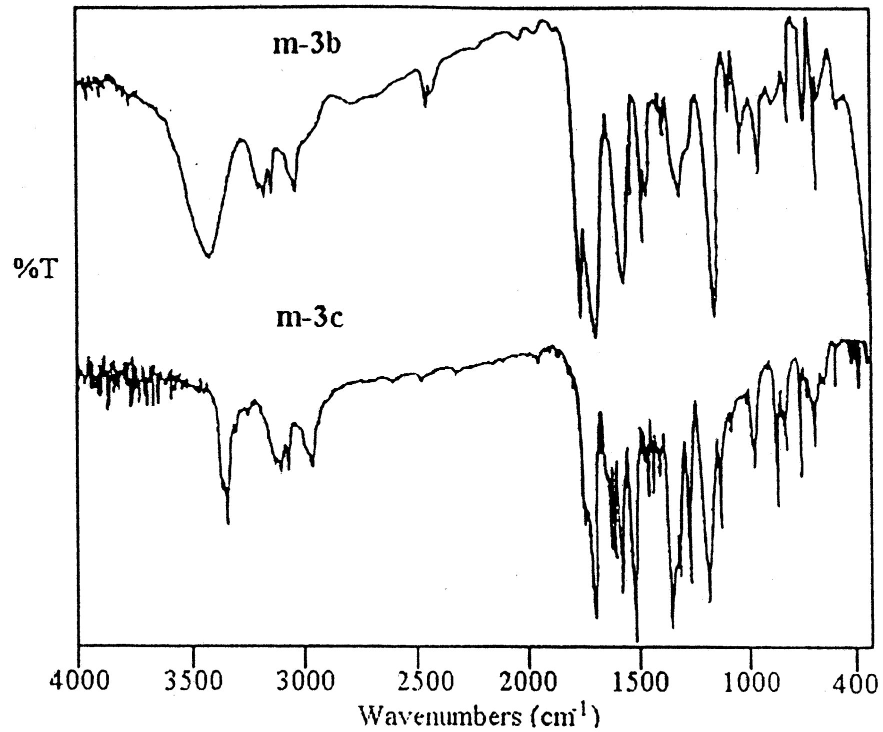


Figure 1. The FT–IR spectra of the monomers m-3b and m-3c.

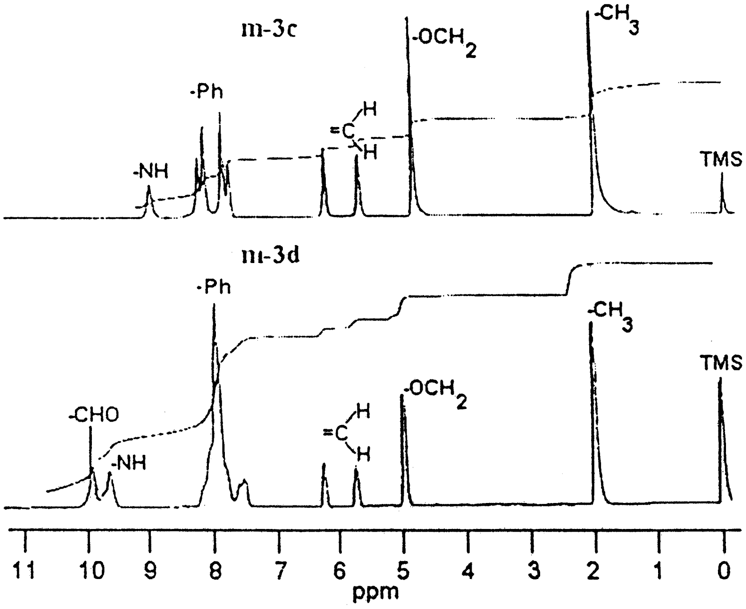


Figure 2. The ^{1}H-NMR spectra of the monomers m-3c and m-3d.

-CONHR functional group. Finally, the band at 1600 cm^{-1} is characteristic of a C=C stretching vibration. The C=0, (-COO-, ester) stretching shifted from 1715 to 1735 cm^{-1} and the C=0, (NH–C=0, amide) stretching shifted from 1680 to 1690 cm^{-1} by conjugation in the FT–IR spectrum of the monomers.

The ^{1}H-NMR spectra of the poly P-3a is shown in Fig. 3.

The ^{1}H-NMR spectrum of P-3a exhibited the corresponding proton signals at 0.8–1.2 due to -CH_3; at 1.3–2.2 due to -CH_2, 4.4–5.2 due to O-CH2, 7.1–8.0 due to the aromatic protons, and at 9.0–9.4 ppm due to the NH protons. The disappearance of 5.7–6.2 ppm peaks (vinylic protons) is as expected.

As summarized in Table 1, the structure of the obtained polymers was confirmed by IR and ^{1}H-NMR spectra.

The main evidence of the polymer is certainly the disappearance of some characteristic signals of the double bond in the spectra, and this fact was effectively observed in our case. Thus, two bands vanished in the IR spectrum: the absorption band at 920 cm^{-1} assigned to the C-H bending of geminal =CH_2 and the stretching vibration band of C=C at 1600 cm^{-1}. From ^{1}H-NMR spectroscopy the formation of the polymer is also clearly evident from the vanishing of the two singlets at 5.7 and 6.3 ppm of the vinyl protons and the appearance of the broad signal at 1.3–2.2 ppm assigned to

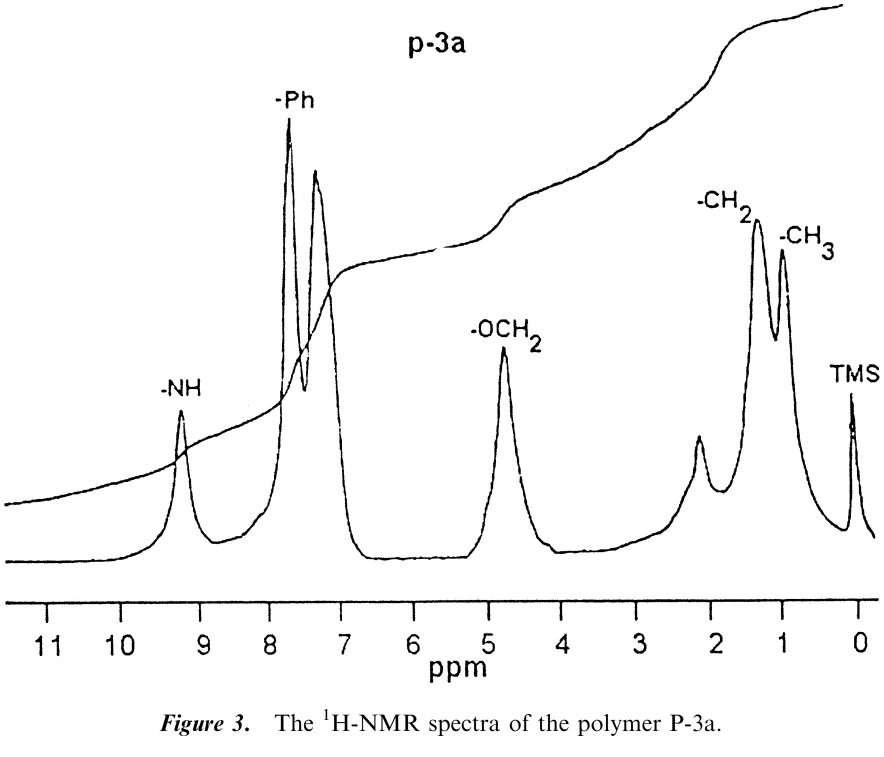


Figure 3. The ^{1}H-NMR spectra of the polymer P-3a.

Table 1. IR and ^{1}H-NMR Spectral Data of the Resulting Polymers

Polymer	IR Spectral Data (film/cm^{-1})	^{1}H-NMR Spectral Data (90 MHz, DMSO-d$_6$, TMS)
P-3a	2690(CH), 1375 (C=O ester), 1690 (C=O, amide), 1590 (C=C aromatic), 1230 (C-O-C ester), 3325 and 1580 (N-H, stretching and bending bands, respectively)	δ (ppm): 0.8−1.2 (-C(CH$_3$)-), 4.4−5.2 (OCH$_2$), 1.3−2.2 (-CH$_2$), 7.1−8.0 (aromatic H), 9.0−9.4 (N-H)
P-3b	2937 (CH), 1730 (C=O ester), 1660 (C=O, amide), 1595 (C=C aromatic), 1228 (C-O-C ester), 3340 and 1640 (N-H, stretching and bending bands, respectively)	δ (ppm): 0.7−1.2 (-C(CH$_3$)-), 4.5−5.2 (OCH$_2$), 1.4−2.4 (-CH$_2$), 7.2−8.1 (aromatic H), 8.8−9.3 (N-H)
P-3c	2956 (CH), 1735 (C=O ester), 1685 (C=O, amide), 1598 (C=C aromatic), 1230 (C-O-C ester), 3280 and 1583 (N-H, stretching and bending bands, respectively), 1510 and 1330 (-NO$_2$, asymmetric and symetric stretching bands, respectively)	δ (ppm): 0.8−1.3 (-C (CH$_3$)-), 4.5−5.3 (OCH$_2$), 1.4−2.2 (-CH$_2$), 7.0−8.0 (aromatic H), 9.0−9.3 (N-H)
P-3d	2953 (CH), 1732 (C=O ester), 1690 (C=O, aldehide), 1692 (C=O, amide), 1600 (C=C aromatic), 1230 (C-O-C ester), 3265 and 1582 (N-H, stretching and bending bands, respectively)	δ (ppm): 0.8−1.3 (-C(CH$_3$)-), 4.4−5.2 (OCH$_2$), 1.5−2.4 (-CH$_2$), 7.1−8.1 (aromatic H), 9.1−9.5 (N-H), 9.7−9.9 (CHO)

an aliphatic-CH$_2$-group. All the other spectroscopic signals for the macromolecule appeared in a normal mode.

The ^{13}C-NMR spectrum of poly P-3a is shown in Fig. 4. The ^{13}C-NMR spectra of the polymers have the characteristic peaks of the monomeric unit. The ester and amide carbonyl of P-3a unit gave lines at 167.1 and 168.8 ppm, respectively. Quaternary carbon of the phenyl ring and meta-, ortho-, and para-carbons of the phenyl ring gave more intense peaks at 130.6, 128.6, 126.7, and 122.3 ppm, respectively. The sharp peak at 65.2 and a less intense peak at 19.8 ppm arose from -OCH$_2$ and -CH$_3$ groups of P-3a. The disappearance of 137.0 and 138.9 ppm peaks (vinylic carbons) is as expected.

Properties of the Polymers

The glass transition temperatures (from DSC thermograms) reported for the polymers are at the glass transition region. In Sch. 2, glass transition temperatures are given comparing these polymers synthesized under the same conditions.

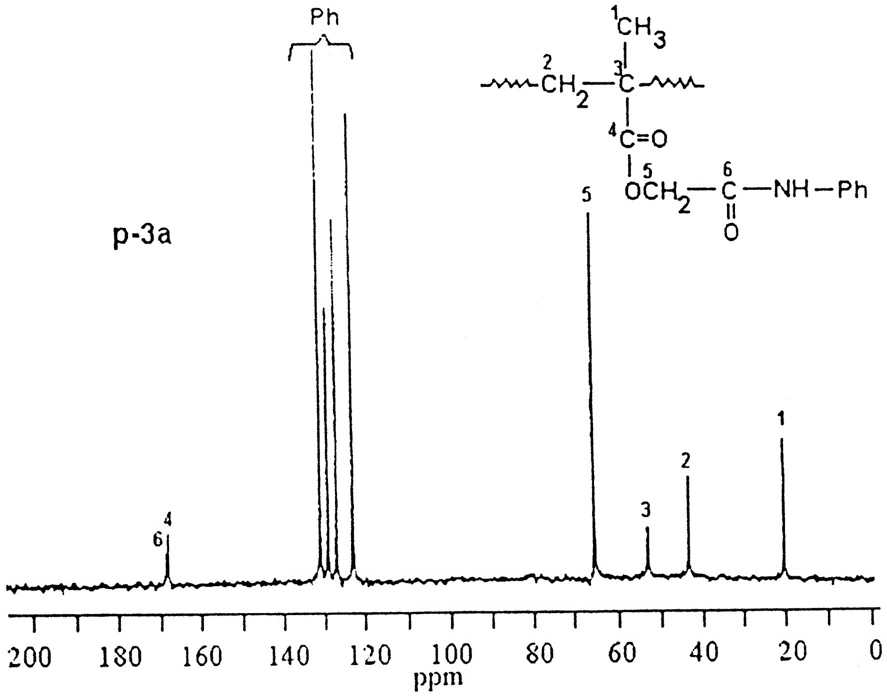
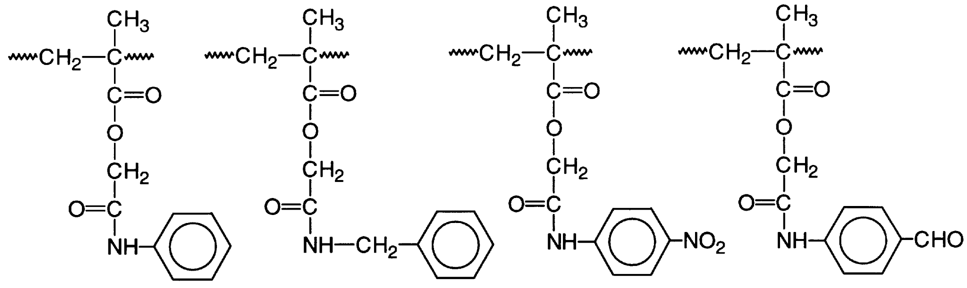


Figure 4. The ^{13}C-NMR spectra of the polymer P-3a.



P-3a
Tg: 79°C

P-3b
Tg: 74°C

P-3c
Tg: 69°C

P-3d
Tg: 84°C

Scheme 2.

The glass transition temperature-(T_g) of all the polymers are approximately the same. The solubility of the resulting polymers is summarized in Table 2. P-3a and P-3d showed excellent solubility in various solvents; however, P-3b and P-3c were not soluble in most solvents.

Table 2. Solubility Data of the Resulting Polymers

Solvent	P-3a	P-3b	P-3c	P-3d
1,4-Dioxane	+ +	+ +	+ +	+ +
DMSO	+ +	+ +	+ +	+ +
Chloroform	−	−	−	− +
Dichlorometan	−	−	−	− +
Aceton	+ +	−	−	+ +
Diethylether	−	−	−	−
n-Hexane	−	−	−	−
Methanol	−	−	−	−
Ethanol	−	−	−	−
THF	+ +	+ −	+ +	+ +
DMF	+ +	+ +	+ +	+ +
MEK	+ −	− +	+ +	+ +

+ + = Soluble at room temperature, + = soluble by heating,
+ − = Swelling or party soluble at room temperature,
− = Insoluble

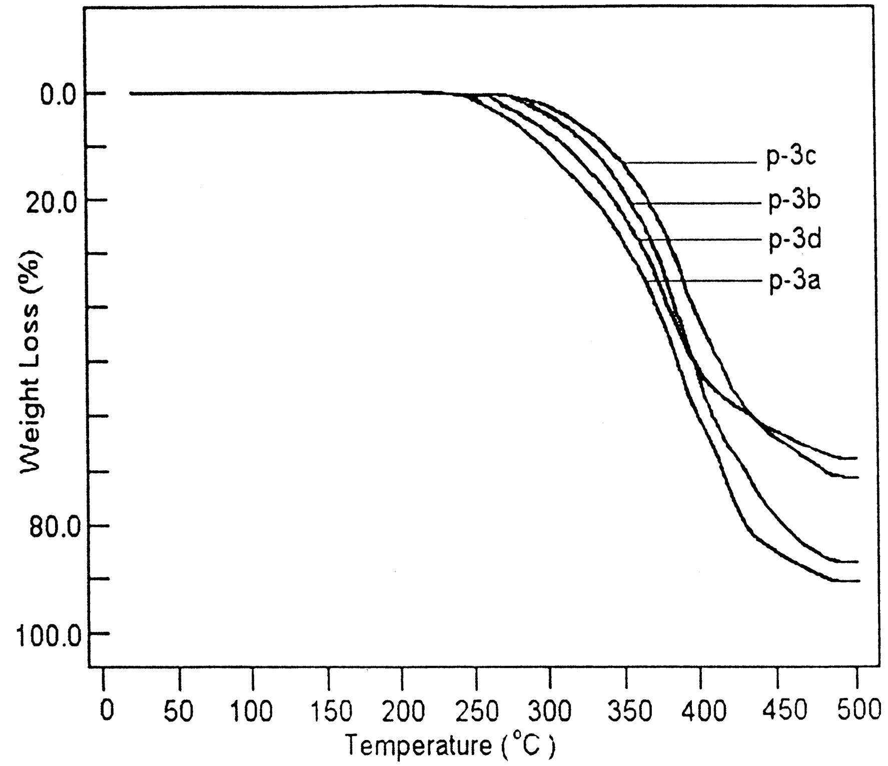


Figure 5. The TGA curves of the polymers.

Thermal and Ultraviolet Stability of the Polymers

The thermal stability of the polymers were investigated by TGA in a nitrogen stream with a heating rate of 10°C/min. Samples weighing not more than 30 mg were cut from the hydrated gelatin sheet and surface water was carefully removed with tissue paper. The weighed samples were placed in a preweighed aluminum sample pan. The samples were cooled to −75°C using liquid nitrogen, then heated up to 500°C, compressed, then quenched at room temperature before carrying out the measurements. In Fig. 5, the TGA thermograms of the polymers are shown. Initial decomposition temperatures of the polymers are similar, which is an important reaction in the degradation of the polymers, at least at the beginning. The results of the thermogravimetric analyses are summarized in Table 3.

The photocrosslinking properties of polymers have been studied by irradiating the polymer films with a high pressure Hg lamp by measuring the changes in the UV absorption intensity at 254 nm. The changes in the UV spectra upon irradiation at 254 nm is extraordinary. After irradiation for 24 hours and 72 hours in the FT–IR spectra, a new band as shoulder at 1701 cm^{-1} was observed on the spectra of the polymers, and absorbance of the shoulder at 1701 cm^{-1} increased relatively as that of the band at 1690 cm^{-1} decreased from 24 hours to 72 hours. In addition, while all the polymers were soluble in 1,4-dioxane, DMSO, DMF, THF, etc. upon irradiation, all the polymers became essentially insoluble in DMSO, DMF, THF, etc., All the experimental data shows that photodegradation at the amide carbonyl region occurred and crosslinking followed. It is known that some polymers having a keto-side chain show photodegradation.[22,23] There is no evidence of the scission of the different side groups because of UV irradiation at 254 nm. However, polymers having cyclobutane rings derived from α-truxillate, β- or δ-truxinates [24] decomposed under irradiation at 250 nm. In addition, some copolyamides, having both a cyclobutane ring and conjugated double band in the main chain decomposed by scission of the cyclobutane

Table 3. TGA Data for the Polymers

Polymer	IDT[a]	Wt. Loss (%) at Temperature (°C) 300	350	400	450	50% Wt. Loss at Temperature (°C)
P-3a	246	11	28	61	84	384
P-3b	271	4	18	55	77	398
P-3c	270	2	13	41	64	415
P-3d	260	8	22	52	61	397

[a] IDT: Initial decomposition temperature.

rings on irradiation at 254 nm or crosslinked via the double bond by irradiation above 310 nm.

CONCLUSION

The synthesis of new methacrylate esters having pendant amide moieties has been reported for the first time. The structure of all the monomers and polymers were characterized by spectroscopic methods. The amide compound includes a ketone group. Ketone polymers are used as photodegradable packaging materials and photoresists for microlithography. The increasing utility of photosensitive polymers in many applications such as microelectronics, printing and UV-curable lacquers, and inks has provided us with an incentive to obtain novel polymers. Thermogravimetric analysis results indicate that the polymers undergo decomposition in two stages. Finally, the photocrosslinking behavior of the polymers were tested as thin films in the presence of UV light.

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