Poly-α-*n*-alkyl Acrylic Derivatives: Synthesis, Influence of Molecuur Weight and *n*-Alkyl Group Length on Physical and Physicochemical Properties

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POLY-α-*n*-ALKYL ACRYLIC DERIVATIVES: SYNTHESIS, INFLUENCE OF MOLECULAR WEIGHT AND *n*-ALKYL GROUP LENGTH ON PHYSICAL AND PHYSICOCHEMICAL PROPERTIES

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ABSTRACT

A series of α-*n*-alkyl acrylic acid monomers was synthesized and homopolymerized by a radical route. Methylation of polyacids using diazomethane led to the corresponding methyl esters and allowed physicochemical analysis. The thermal stability of polyacids and polymethyl esters is insensitive to the nature of the alkyl group and to the molecular weight. The glass transition temperature, T_g, classically decreases with increases in alkyl group length such as alkyl polymethacrylates. Molecular weight has a drastic influence on T_g for short alkyl groups.

INTRODUCTION

The first terms of poly-α-n-alkyl acrylic derivatives (R = H, CH_3, and C_2H_5; Fig. 1) have largely been depicted in the literature [1–6].

For higher terms, very few studies have been reported. In the case of methyl ester monomers [7–10], Chikanishi and Tsuruta [7] prepared and anionically polymerized two α-n-alkyl acrylic methyl esters (R = C_3H_7, C_4H_9) at −78°C. Attempts to initiate polymerization of these monomers with radical initiators resulted in either very low molecular weight polymers or no polymer at all. In the same way, Gisser and Mertwoy [8] synthesized and also anionically polymerized the $C_{12}H_{25}$, $C_{16}H_{33}$, and $C_{18}H_{37}$ terms. They claimed that α-n-alkyl acrylates (R $\geq$ $C_{12}H_{25}$) homopolymerized only if prepared by a method that yielded pure isomer-free monomer. Therefore, they used the Chikanishi synthesis which combines extension of the carbon skeleton with the introduction of the ethylenic group on a specific position, thereby yielding an unambiguous product.

There were even fewer results for homopolyacids. Hastings [11] reported that free radical homopolymerization of α-n-alkyl acrylic acids was not successful. Nevertheless, Cheng et al. [12], who synthesized two α-n-alkyl acrylic acids (C_3H_7, C_4H_9) by using the Chikanishi method, homopolymerized these monomers with AIBN as initiator. Finally, we mention the particular polymerization of the $C_{18}H_{37}$ term using γ-irradiation of a Langmuir–Blodgett layer [13].

We chose to fill this gap by the synthesis and study of a series of homopolyacids (R' = H; R = C_3H_7, C_5H_{11}, C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{18}H_{37}$) polymerized by a radical route. Moreover, we also had access to the corresponding methyl ester derivatives by quantitative modification of carboxylic groups.

In this paper, we first report the monomer synthesis, radical polymerization, and physicochemical properties of polyacids and methyl ester derivatives. Second, we focus on the influence of alkyl groups and polymer molecular weights on glass transition temperature and thermal stability.

EXPERIMENTAL

Materials

Diethylmalonate (Aldrich), formaldehyde (37% in water; Aldrich), n-alkyl bromine (Aldrich) Diazald (Aldrich), and diethylamine (Janssen) were used without further purification.
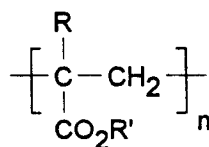

FIG. 1.   Structural formula of poly-α-n-alkyl acrylic derivatives.

TABLE 1. Diethyl n-Alkylmalonates

R	bp, °C	p, torr	Yield, %
C_3H_7	58	0.07	82
C_5H_{11}	90	0.2	97
C_8H_{17}	130	0.1	95
$C_{10}H_{21}$	116	0.05	88
$C_{12}H_{25}$	138	0.05	98
$C_{18}H_{37}$	37 (mp)	–	97

Monomer Synthesis

Diethyl n-Alkylmalonate, 1

Diethyl n-alkylmalonate was prepared by adding a solution of sodium ethoxide (0.5 mol) in 300 mL ethanol to a mixture of diethylmalonate (0.84 mol) and alkyl bromide (0.2 mol). The reaction mixture was then refluxed for 5 hours. The resulting solution was evaporated to dryness in vacuo and yielded a residue which was dissolved in 300 mL water and 100 mL diethylether. The aqueous solution was separated and washed twice with 50 mL diethylether. The organic layers were put together and dried over anhydrous $MgSO_4$. After filtering, the ether was evaporated off. The residual diethylmalonate was eliminated in vacuo, and the product was distilled under reduced pressure, except for the C_{18} term for which a white solid was obtained (Table 1).

n-Alkylmalonic Monoethyl Ester, 2

Monoethyl ester was prepared by adding a solution of potassium hydroxide (9.4 g) in 160 mL (300 mL for C_{18}) ethanol to 0.163 mol of 1 in 20 mL (200 mL for C_{18}) ethanol. The mixture was stirred at 0–10°C (room temperature for C_{12} and 30°C for C_{18}) for 24 hours and evaporated to dryness in vacuo. To the residue, 300 mL (4 L for C_{18}) water was added. For C_3 to C_{10} terms, the solution was washed twice with diethylether (50 mL), separated, and then acidified with 3 N HCl to pH 1. The monoester was extracted twice with diethylether (100 mL). For C_{12} to C_{18} terms, the aqueous solution was acidified with 3 N HCl to pH 1 while stirring; the monoester precipitated. The precipitate was filtered, washed with water, and dissolved in diethylether. In all cases the organic layers were put together, washed with water, and dried over anhydrous $MgSO_4$. After filtering and evaporation, a colorless oil (C_3, C_5, C_8, and C_{10} terms) or a white powder (C_{12} and C_{18}) was obtained in good yield (Table 2). The crude products were used without further purification for the following step.

TABLE 2. n-Alkylmalonic Monoethyl Esters

R:	C_3H_7	C_5H_{11}	C_8H_{17}	$C_{10}H_{21}$	$C_{12}H_{25}$	$C_{18}H_{37}$
Yield, %:	79	88	84	83	95	89

Ethyl α-n-Alkylacrylate, 3

To **2**, 0.128 mol diethylamine and 0.162 mol formaldehyde (37% in water) were added slowly at 0–5°C (50°C for C_{12} and C_{18}). The mixture was then stirred for 24 hours at room temperature (30°C for C_{12} and C_{18}). For the C_3 to C_{10} terms, 200 mL water was then added to the reaction mixture. In all cases the two distinct layers were separated and extracted once with diethylether (200 mL). After separation, the organic layer was cooled with ice and acidified with 1 N HCl to pH 1. The separated organic layer was first washed with water (50 mL) and then with a saturated NaCl aqueous solution; it was then dried over anhydrous $MgSO_4$. After filtering and evaporation, a colorless oil was obtained and distilled under reduced pressure (Table 3). Only the C_{18} term crystallized (mp = 38°C).

α-n-Alkylacrylic Acid, 4

α-n-Alkylacrylic acid was prepared by adding a solution of 1 N potassium hydroxide (125 mL) at 5°C to a solution of **3** in 140 mL ethanol. The reaction mixture was then stirred for 20 hours at room temperature. The ethanol was evaporated off in vacuo, and the aqueous layer was diluted with water and washed twice with diethylether (50 mL). The solution was then cooled with an ice bath and acidified with 1 N HCl to pH 1. For the C_3 to C_{10} terms, the product was extracted twice with diethylether (50 mL). For C_{12} to C_{18}, the acid which precipitated during acidification was washed with water and dissolved in diethylether. In all cases the organic layer was first washed with water and then with a saturated NaCl aqueous solution. After drying over anhydrous $MgSO_4$, filtering, and evaporation in vacuo, we obtained a colorless oil which we distilled under reduced pressure for C_3 to C_{10} or a white solid for C_{12} and C_{18} (Table 4).

FT-IR and H^1-NMR spectra verified the corresponding structures. The purity of the monomers was verified by gas chromatography and estimated to be better than 99.9%.

Polymer Synthesis

Radical polymerizations were carried out in bulk using azo-bis-isobutyronitrile (AIBN) as initiator. In a typical experiment, 1 g of monomer and AIBN (0.5 to 5% molar with respect to monomer) were introduced into a glass tube and thoroughly out-gassed overnight under nitrogen at room temperature. Polymeriza-

TABLE 3.   Ethyl α-n-Alkylacrylates

R	bp, °C	p, torr	Yield, %
C_3H_7	45	8	78
C_5H_{11}	34	0.01	74
C_8H_{17}	76	0.05	88
$C_{10}H_{21}$	88	0.05	78
$C_{12}H_{25}$	83	0.01	86
$C_{18}H_{37}$	130	0.01	67

TABLE 4.   α-*n*-Alkyl Acrylic Acids

R	bp, °C	*p*, torr	Yield, %
C_3H_7	46	0.01	80
C_5H_{11}	102	3	87
C_8H_{17}	100	0.5	93
$C_{10}H_{21}$	95	0.1	90
	mp, °C		
$C_{12}H_{25}$	43		94
$C_{18}H_{37}$	65		70

tion was allowed to proceed for 24 hours (72 hours for C_{10} and C_{12} terms) with stirring at 50°C (60°C for C_{10} and C_{12}). Purification was completed by two further reprecipitations into 50 mL methanol from 5 mL DMF solution of the solidified mixture, after which the polymer was dried in vacuo at 40°C for 48 hours.

For the C_{18} term, benzoyl peroxide was used as the initiator at 80°C for 120 hours with the same procedure.

Polymer Modification

Quantitative methylation of poly-α-*n*-alkylacrylic acids was carried out by using diazomethane as the reagent. Typically, a 15-mL diethylether solution of diazomethane, ready for use, was classically prepared by adding an alcoholic solution of KOH (1 g KOH to 1 mL H_2O and 4 mL EtOH) to 300 mg Diazald. The yellow solution was poured onto 0.5 g polymer with stirring. Solubilization occurred progressively with methylation, and discoloration was observed. The procedure was repeated until the solution remained yellow. After evaporation of diethylether, the polymer was twice precipitated into methanol from chloroform solution and dried in vacuo at 40°C for 48 hours.

Characterization Techniques

Size Exclusion Chromatography (SEC)

The average molecular weight was computed from chromatograms obtained by using a Waters 510 Gel Permeation Chromatograph with polystyrene standards. The apparatus was equipped with five μStyragel columns, 100, 500, 10^3, 10^4, and 10^5 Å, working in toluene. Detection was with a R 401 Waters refractometric detector.

Gas Chromatography (GC)

A Perkin-Elmer Autosystem gas chromatograph was used with a SGE widebore column 25 QC 5/BP 1 1.0 and a flame ionization detector. The oven temperature program was as follows: 1 minute at 80°C, a temperature increase from 80 to 220°C at 20°C/min, and 220°C for 15 minutes.

Differential Scanning Calorimetry (DSC)

DSC was used to determine the glass transition temperature (T_g) of the polymer by using a Perkin-Elmer DSC-7. The reported T_g was taken as the midpoint of the curve. The heating rate was 20°C/min, and the sample weight was about 10 mg. Calibration was achieved with indium as the reference material. In all experiments the samples were first heated above T_g to remove the thermal history before cooling.

Thermogravimetric Analysis (TGA)

Polymer thermal stability was followed by thermogravimetric analysis (TGA-7, Perkin-Elmer). Experiments were carried out under an N_2 atmosphere on samples of about 10 mg at a heating rate of 20°C/min from 100 to 550°C.

RESULTS AND DISCUSSION

Monomer Synthesis

Several authors have synthesized a number of α-n-alkylacrylic derivatives as reactive intermediates by very different routes [14–21] without attempting to homopolymerize them or without success [11]. The authors who homopolymerized these monomers used the synthetic route proposed by Chikanishi [7]. We also followed this route by using ethyl ester derivatives instead of the commonly reported methyl esters (Scheme 1). After four steps the monomers were obtained with an overall yield of from 40 to 75% according to the alkyl group.

Homopolymerization

Homopolymers were prepared in bulk with AIBN as initiator from α-n-alkylacrylic acids. The resulting polymers were soluble in DMF, pyridine, and hot DMSO but insoluble in water. This water insolubility was previously mentioned
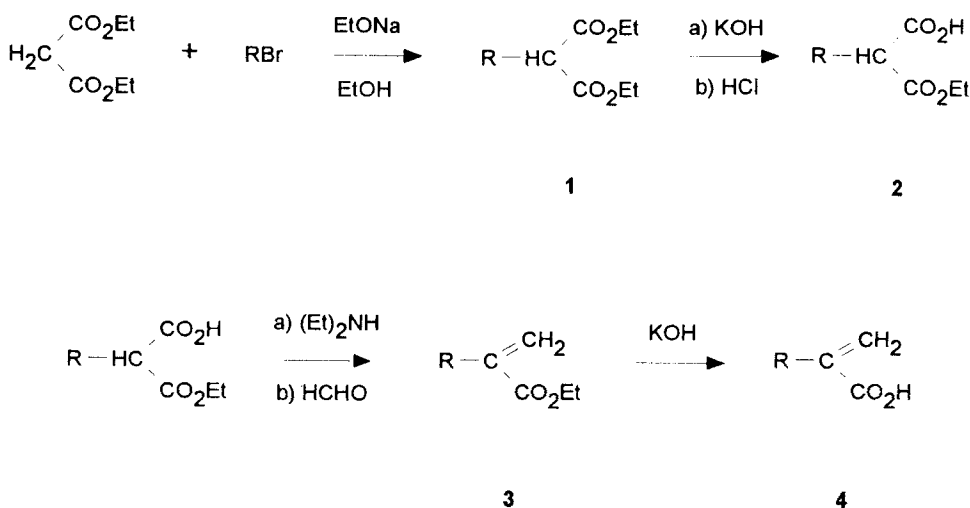
SCHEME 1.

[22] for poly-α-ethyl acrylic acid of high molecular weight. For this reason, physico-chemical characterization was performed on methyl ester derivatives obtained by chemical modification with diazomethane. This type of esterification was also reported to be necessary by Tirrell [23] for NMR analysis of poly-α-ethyl acrylic acid. SEC chromatograms were carried out in toluene. The average molecular weights of the samples studied were in the 2,000 to 60,000 range depending on the alkyl group. An overall yield of precipitated polymer in the 35 to 52% range was obtained.

In the following sections PnA and PnM represent polyacids and methylated polymers bearing a linear alkyl group of n carbons, respectively.

Thermal Properties

Thermal stability was measured by thermogravimetric analysis on acid and methyl ester homopolymers. Homopolyacid thermograms were similar, whatever the nature of the alkyl group and the average molecular weight (e.g., Fig. 2 for P3A and P12A).

Polyanhydride formation occurs above 170°C as shown by a decrease of weight due to a loss of water. Degradation starts at about 350°C, with a maximum at 425°C according to the first derivative curve.

In the case of methyl ester homopolymers, the thermograms are identical whatever the average molecular weight. A slight increase of degradation tempera-
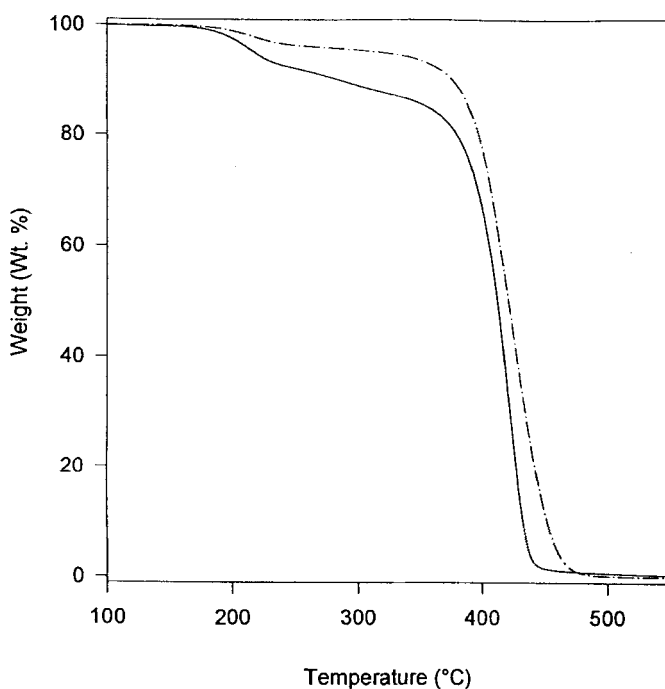

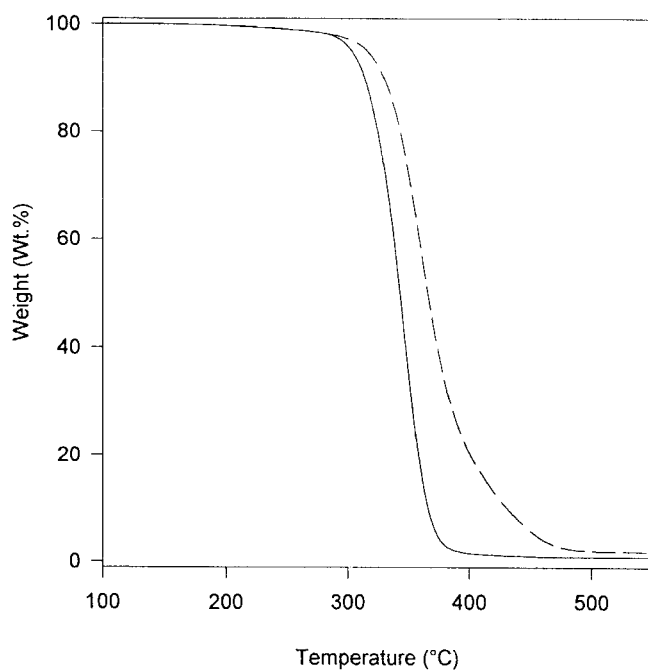FIG. 2. Thermogravimetric analysis of homopolyacids; e.g., (———) P3A, ($-\cdot-$) P12A.

FIG. 3.   Thermogravimetric analysis of methylated homopolymers; e.g., (——) P3M
$\overline{M}_n = 27,000$), (− −) P12M ($\overline{M}_n = 13,000$).
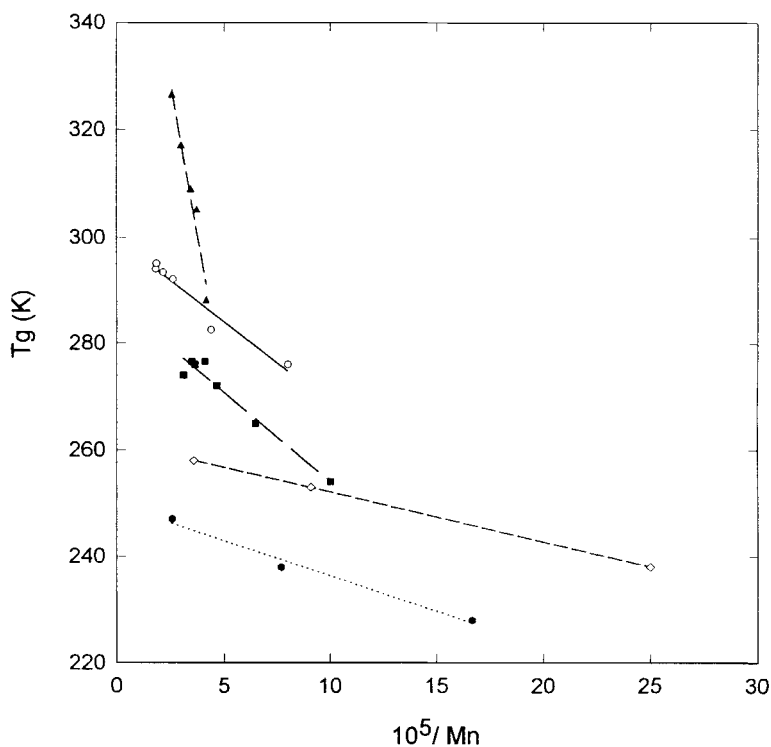
FIG. 4. T_g versus $10^5/\overline{M}_n$: (▲) P3M, (○) P5M, (■) P8M, (◇) P10M, (●) P12M.

TABLE 5. K and T_g^∞ Values Determined from Eq. (1) and Fig. 4

	P3M	P5M	P8M	P10M	P12M
$K \times 10^{-5}$	-22.5	-3.1	-3.3	-0.9	-1.3
T_g^∞, K	384	299	287	261	249

ture is noticed as the alkyl group becomes longer [e.g., Fig. 3 for P3M ($\overline{M}_n$ = 27,000) and P12M ($\overline{M}_n$ = 13,000)]. Degradation begins at about 280–300°C, with a maximum at 340–360°C according to alkyl group. Cheng et al. [12] reported similar results for P2M and P3M.

Glass Transition Temperature

No T_g could be observed for polyacids because of anhydride formation. Thus, T_g is expected to be higher than for methylated polymers.

Influence of molecular weight on the T_g for methyl ester homopolymers is depicted in Fig. 4 and is well represented by the following equation:
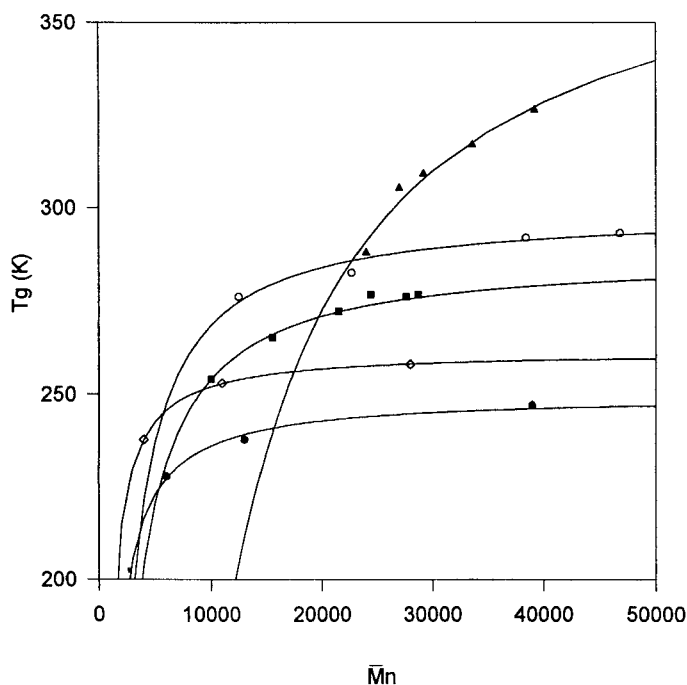
$$T_g = T_g^\infty + \frac{K}{M_n} \tag{1}$$

FIG. 5. T_g versus $\overline{M}_n$: (▲) P3M, (○) P5M, (■) P8M, (◇) P10M, (●) P12M. (——) Computed curves using Eq. (1) and Table 5 values.
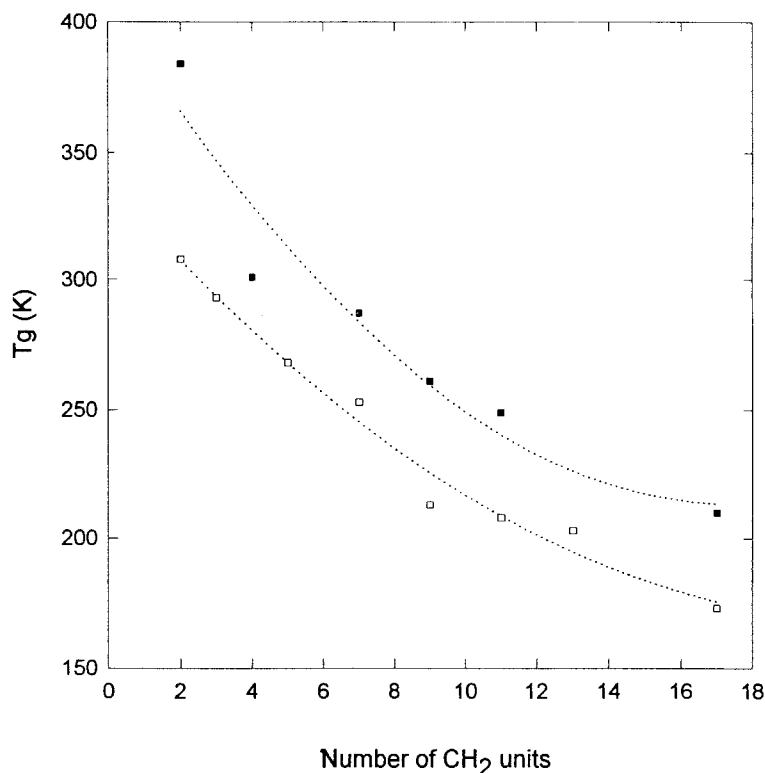
FIG. 6. T_g versus number of methylene units for ($\square$) poly(n-alkyl)methacrylates [1] and ($\blacksquare$) PnM.

which allowed us easy access to T_g^∞ and K for the different terms (Table 5).

The classical increase of T_g with $\overline{M}_n$ is represented on Fig. 5 where the experimental points and the theoretical curves obtained from T_g^∞ and K values, as above mentioned, are in good agreement.

It is well-known that when the alkyl group length decreases or $\overline{M}_n$ increases, the resulting T_g increases. In our case, for P5M to P12M, the influence of $\overline{M}_n$ decreases rapidly and a plateau is obtained beyond 15,000. On the other hand, a tremendous effect is observed up to 60,000 for P3M. This observation is very significant and can explain the great difficultly in comparing the different results reported in the literature, especially for short alkyl groups and when no information about the molecular weight is mentioned. To these disadvantages we must add the knowledge of experimental conditions necessary for T_g determination: thermal history, cooling rate, starting temperature, physical aging time, heating rate, choice of experimental measurement (middle point or onset of the curve)—so many parameters which lead to values which can differ up to several tens of degrees [24].

If we consider T_g^∞, the influence of the length of R is shown on Fig. 6. Notice that the evolution of T_g^∞ with R is very similar to that for polyalkyl methacrylates [1] if we assume that these values can be compared; that is, if the molecular weights are high enough to relate T_g to T_g^∞.

CONCLUSION

In this paper we have shown that the length of *n*-alkyl groups in poly-α-*n*-alkylacrylic acids or methylated derivatives has very little influence on polymer thermal stability. Nevertheless, a decrease of T_g is observed according to free volume theory. The drop in T_g with molecular weight clearly shows one of the difficulties in comparing different results. However, other parameters are very important for T_g measurements. An investigation on how to understand the effects of such parameters as aging time, aging temperature, and heating rate is now under way.

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