Copolymers of Methyl Methacrylate and Acrylate Comonomers: Synthesis and Characterization

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SYNOPSIS

Methyl methacrylate (MMA) has been copolymerized with *n*-butyl acrylate (*n*-BA), ethyl acrylate (EA), and 2-ethylhexyl acrylate (2-EHA) in solution at 70°C using benzoyl peroxide as free radical initiator. The copolymer composition was estimated by the ^{1}H-NMR spectroscopic technique. The copolymers were further characterized by IR, XRD, TGA, DTA, DSC, GPC, and solubility. The adhesive characteristics of the copolymers to cellulosic substrate are also reported. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The copolymers consisting of acrylic and methacrylic esters have achieved prime importance due to their versatile applications.[1-3] A vast patent literature[4,5] is available on adhesive applications of copolymers. The use of acrylic based adhesive for cellulosic substrates such as hard board, plywood, particleboard, etc. is well known.[6] Mclaren[7] reported the adhesion of high polymers based on methyl methacrylate (MMA) to cellulosic substrates and the influence of structure, polarity, and tack temperature on adhesion. Mao and Reegan[8] studied the effect of acrylate content on the adhesive strength (peel strength) of copolymers in systems based on MMA with ethyl acrylate (EA) and butyl acrylate (BA). Dhal et al.[9] studied the terpolymers based on *n*-butyl acrylate (*n*-BA), acrylic acid (AA), and hydroxy acrylates as efficient pressure-sensitive adhesives and investigated the effect of the concentration of these polar monomers on tape performance. The structural information and the adhesive applications of the polymer material cannot be confirmed without proper analysis and characterization.[10] A voluminous work has been carried out on the copolymers of MA and various acrylate comonomers with respect to their syntheses, characterization, and end uses.[8,10-13] However, the earlier studies were mainly confined to low conversion.

As part of the general program of the study of acrylic copolymers at high conversion, the copolymerization of MMA with acrylate comonomers by free-radical polymerization technique is reported in the present study. The copolymers have been characterized by ^{1}H-NMR, IR, x-ray diffraction (XRD), gel permeation chromatography (GPC), thermogravimetric analysis (TGA), dynamic thermal analysis (DTA), differential scanning calorimetry (DSC), and solubility behavior. The adhesive properties of these copolymers to cellulosic substrates were also studied.

EXPERIMENTAL

Materials and Copolymerization

The monomers MMA, *n*-BA, EA, and 2-ethylhexyl acrylate (2-EHA) were obtained from fluka and freed from inhibitor by washing with 10% sodium hydroxide solution, then with distilled water, and drying over anhydrous calcium chloride. The purified monomers were distilled under reduced pressure over 4 Å molecular sieves (E. Merck, Germany). Benzoyl peroxide (Robert Johnson) was purified by recrystallization from methanol and a stock solution was made with chloroform. All solvents used were reagent grade obtained from BDH and were purified by the standard procedure.[14]

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Table I Copolymerization of MMA with Acrylate Comonomers

Sr. No.	Polymer Code	Monomer (M1) (mol)	Comonomer (M2) (mol)	Solvent (mol)	Conversion (%)
1	MEA 11	0.046	0.046	0.106	95.1
2	MEA 12	0.028	0.056	0.095	95.4
3	MEA 13	0.028	0.084	0.127	98.2
4	MEA 21	0.074	0.037	0.127	97.1
5	MEA 31	0.082	0.028	0.125	96.5
6	MBA 11	0.028	0.028	0.072	97.7
7	MBA 12	0.028	0.056	0.112	96.5
8	MBA 13	0.019	0.056	0.102	97.9
9	MBA 21	0.070	0.035	0.130	95.2
10	MBA 31	0.084	0.028	0.135	95.3
11	MEHA 11	0.037	0.037	0.120	96.2
12	MEHA 12	0.019	0.033	0.099	97.2
13	MEHA 13	0.011	0.033	0.086	97.9
14	MEHA 21	0.046	0.023	0.101	96.5
15	MEHA 31	0.057	0.019	0.105	95.2

Polymerization conditions: monomer (M1), methyl methacrylate (MMA); comonomer (M2), ethyl acrylate or butyl acrylate or 2-ethylhexyl acrylate; temperature, 70 ± 0.1°C; period of polymerization, 6 h; solvent, ethyl acetate; nonsolvent, petroleum ether.

The polymerization[15] was carried out in a two-necked reaction flask equipped with a condenser and nitrogen gas inlet. A predetermined amount of MMA, acrylate comonomer, ethyl acetate, and benzoyl peroxide were charged into a reaction flask (Table I). The flasks were placed in an electrically controlled water bath at 70 ± 0.1°C with constant stirring. The proper time of copolymerization, i.e., the time necessary to polymerize more than 95% of the reaction mixture was found by trial and error. After the desired conversion, the reaction was stopped by adding an excess of dry petroleum ether. The precipitated polymers were filtered and further purified by repeated reprecipitation from ethyl acetate into petroleum ether to remove unreacted comonomers and initiator species. The purified polymers were dried in vacuum at 35°C to constant weight for several hours. The experimental conditions and results of copolymerization are summarized in Table I.

CHARACTERIZATION OF COPOLYMERS

The composition of the copolymers was determined by ^{1}H-NMR technique. The ^{1}H-NMR spectra were recorded using a Varian 60 MHz spectrophotometer. Samples were used in the form of solution (10–15% w/v) in carbon tetrachloride (spectroscopic grade) at ambient temperature. Tetramethyl silane (TMS) was used as internal standard.

A thin film of polymer solution (0.5 mg/mL) in spectroscopic grade chloroform was cast on a KBr pellet, used for recording IR spectra of copolymers, on a Perkin–Elmer 781 IR spectrophotometer.

Nickel filtered copper radiation (λ = 0.15404 nm) operated on an X-ray diffractometer (model Rigaku D/max-IIIB) was used as a source under the operational conditions of 30 kV and 20 mA. XRD of the film coated on a glass slide was scanned at the full range from 5 to 70°.

GPC experiments were carried out on a Waters Associates Pump (730 Datamodule) at ambient temperature. The detailed conditions and calibration chart for the GPC experiment are as follows:

1. columns: styragel (10^5, 10^4, 10^3 Å);
2. solvent: dry tetrahydrofuran (THF);
3. flow rate: 1.5 mL/min;
4. detector: refractive index;
5. sample size: 100 μL;
6. standards: polystyrene (390, 240, 100, 35, 8.5) $\times 10^3$;
7. chart speed: 0.80 cm/min;
8. accuracy: ±6%;

Calibration Chart

Retention Time (min)	Molecular Weight ($\times 10^{-3}$)
13.05	390
13.60	240
14.97	100
16.57	35
18.27	8.5

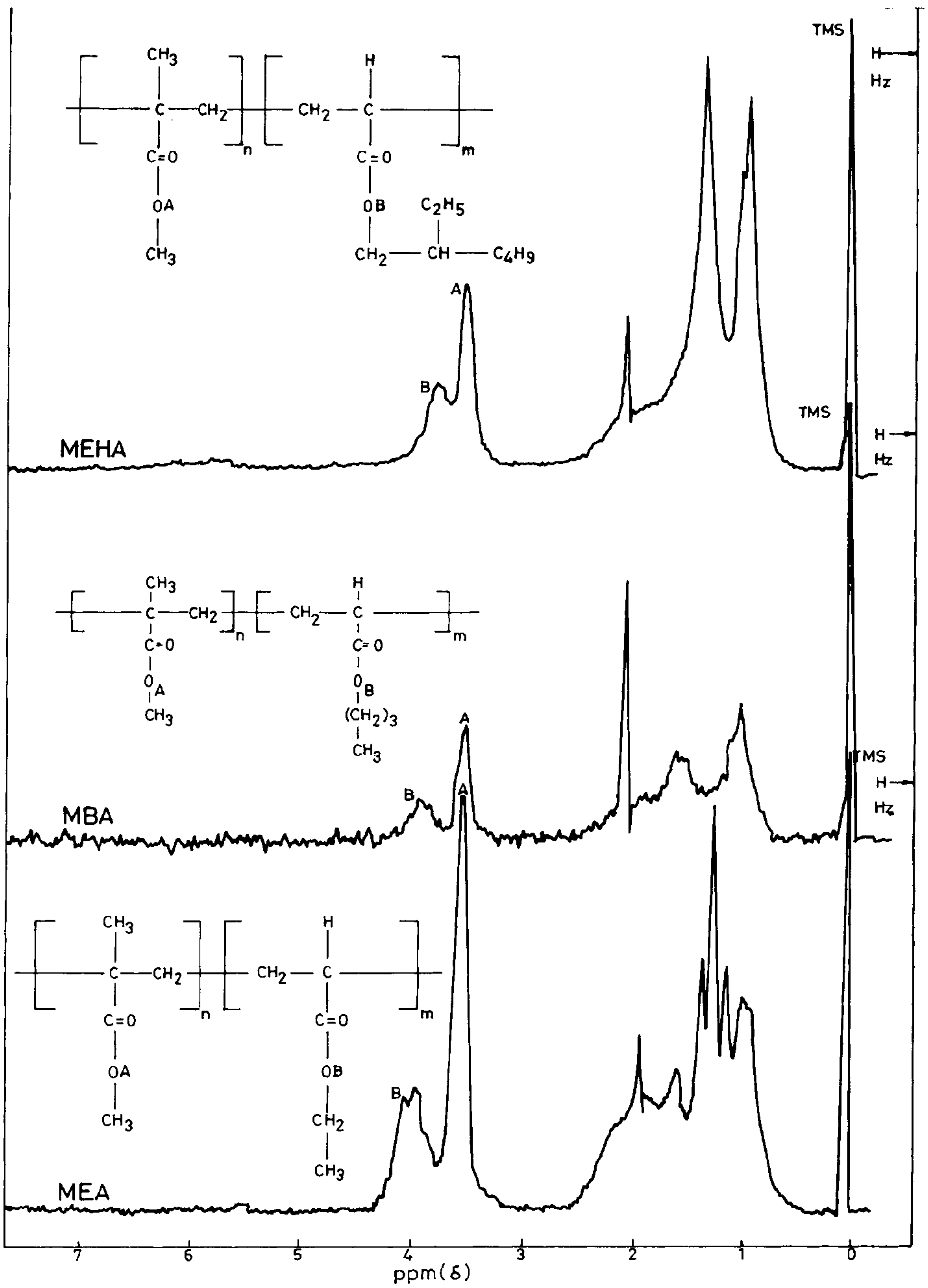

Figure 1 ^{1}H-NMR spectra of copolymers of methyl methacrylate with acrylate comonomers.

The solubility of copolymers were checked in various polar and nonpolar solvents for the information about the solubility behavior of the copolymers.

The thermal stabilities of the copolymers were determined by TGA. The TGA of the copolymers was carried out using a Shimadzu DT/10 Thermal Analyzer in a nitrogen atmosphere from ambient to 500°C at a heating rate of 10°C/min.

The differential thermograms of the copolymers were recorded on Stanton Redcraft STA-

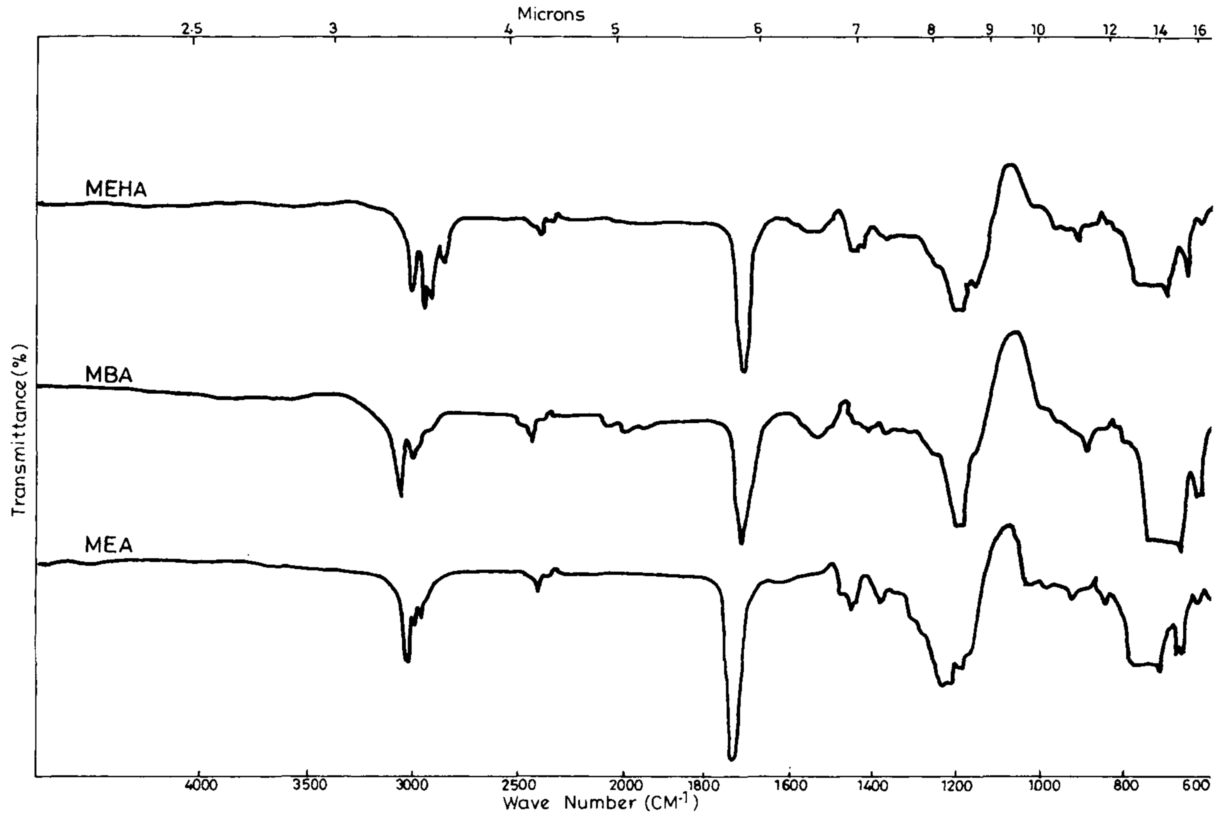

Figure 2 IR spectra of copolymers of methyl methacrylate with acrylate comonomers.

780 series Differential Thermal Analyzer with a CPC-706 temperature programmer in a nitrogen atmosphere from ambient to 500°C at a heating rate of 10°C/min. The glass-transition temperatures (T_g) of the copolymers were determined by DSC analysis on a Dupont 990 Thermal Analyzer. The samples were cooled to liquid nitrogen temperature and the experiments were carried out by programmed heating at the heating rate of 5°C/min.

The adhesive properties of the copolymers were studied from the adhesive strength measured in terms of peel adhesion. For this purpose, the copolymers were coated to polyester film to a thickness of 0.3 mm and dried in an oven at 70–75°C for 30 min to ensure the complete removal of solvent. These specimens were finally subjected to a standard tape adhesion test. The 180° peel adhesion[16] was carried out using an Instron 1026 Universal Testing Machine at a crosshead speed of 500 mm/min. A plain wooden surface was used as the substrate instead of stainless steel. The results reported are the average of four trials.

RESULTS AND DISCUSSION

All the newly synthesized copolymers were in general sticky, transparent, colorless solids. However, the copolymers of MMA and 2-EHA were observed to be semisolid exhibiting a most tacky nature. The representative ^{1}H-NMR, IR, X-ray spectra, and TGA, DTA, and DSC thermograms of the copolymer systems (1 : 1 molar ratio) under study are exhibited in Figures 1–6, respectively.

^{1}H-NMR Spectroscopy

The nonappearance of peaks due to unsaturated protons between 5 and 6 ppm indicates the absence of monomer impurities. It is well known that the relative integral intensities of peaks due to comonomers are directly proportional to the copolymer composition.[11] The peaks at 3.5 and 3.8 ppm are due to $-OCH_3$ of MMA and $-OCH_2$ of acrylate comonomers, respectively. The integral intensities of the peaks were used to estimate the copolymer composition. The results of copolymer

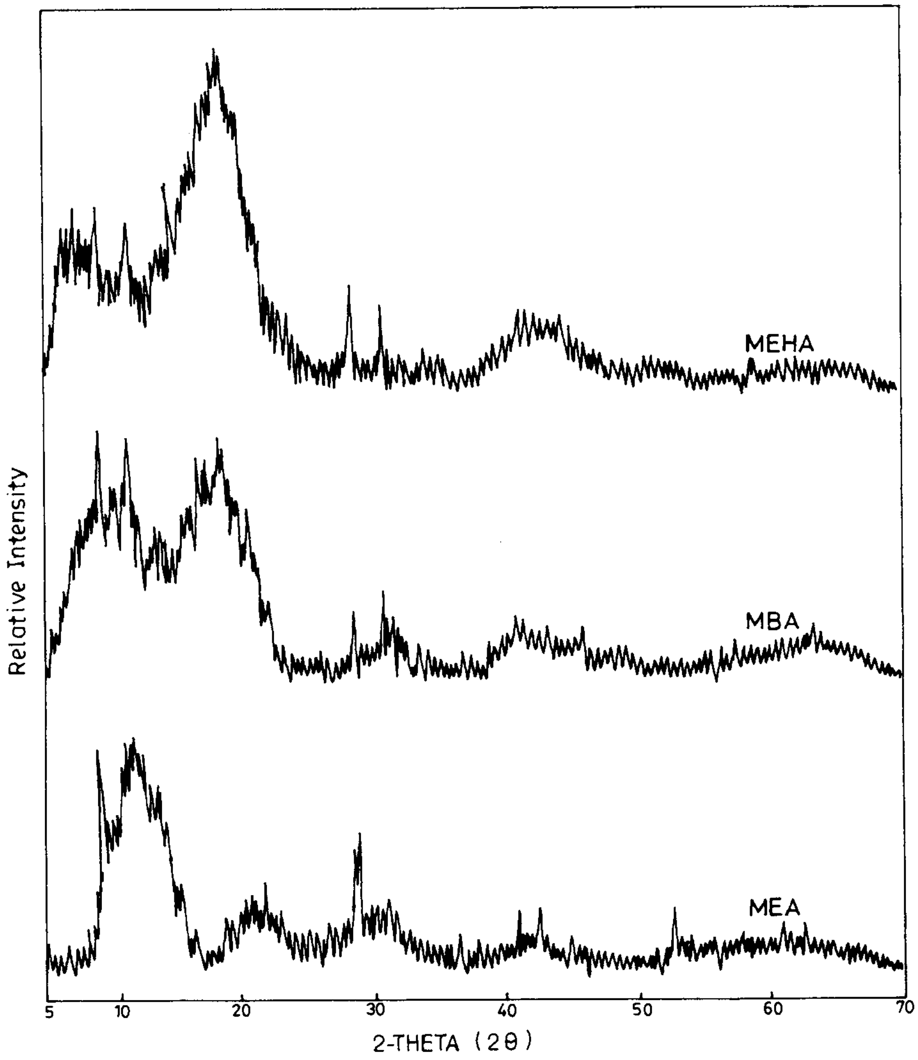

Figure 3 X-ray diffraction patterns of copolymers os methyl methacrylate with acrylate comonomers.

composition of various copolymer systems obtained by ^{1}H-NMR analysis are summarized in Table II.

IR Spectroscopy

The IR spectral pattern of all the copolymers in a given series was almost similar. However, the nonappearance of a band at 1600 cm^{-1} in each case clearly indicated the absence of monomer impurities. The bands due to the carbonyl group of MMA and acrylate comonomers appear to have overlapped at 1730–1740 cm^{-1} (Fig. 2). Therefore, it was not possible to determine copolymer composition.

Crystallinity

The XRD pattern was in general amorphous in nature. However, the copolymer composition and the alkyl side group appear to have no effect on the crystallinity of the copolymers under similar experimental conditions (Fig. 3). All the copolymer systems showed three to four peaks. The first peak in all cases occurs at approximately the same θ value whereas the other peaks occurred at different θ values, which may be due to the low degree of crystallinity.[17]

GPC

GPC data are summarized in Table III. It is clear from the results that the copolymers are of high

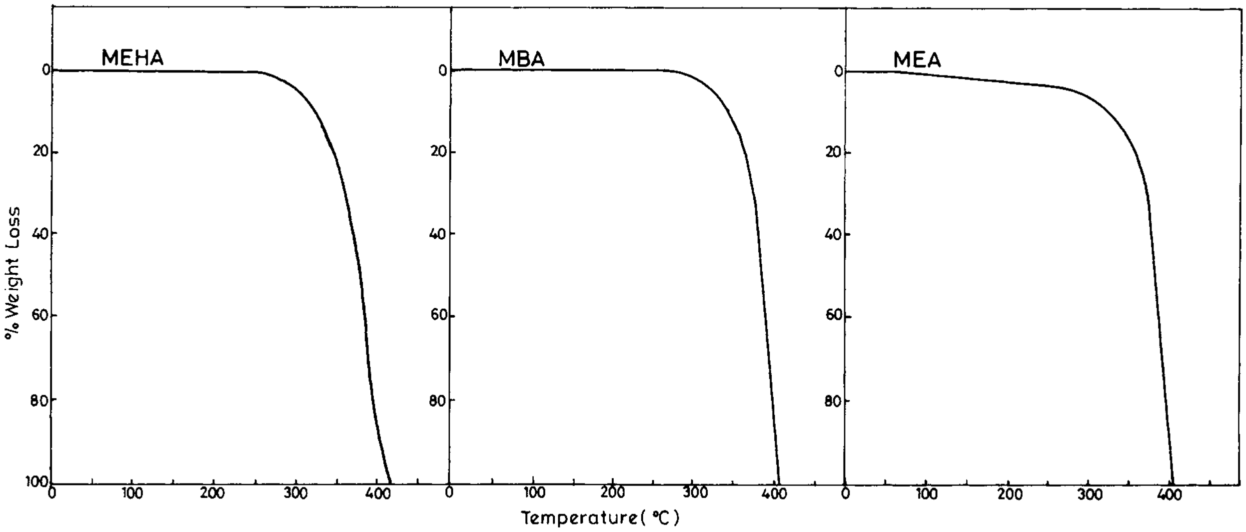

Figure 4 TGA plots of copolymers of methyl methacrylate with acrylate comonomers.

molecular weights and broad molecular weight distribution. In the copolymer systems under study, it is well established that the reactivity of MMA is much higher than its comonomers; hence the high MMA content results in the copolymer. As the overall conversion is regulated around 95% or more in all the copolymer systems studied, a more or less similar pattern of molecular weight distribution is observed.

The molecular weight of the copolymers of MMA and other acrylate comonomers remains almost unaffected by increasing the MMA content. However, as expected, the molecular weight changes in the upward direction with an increase in the content of acrylate comonomers keeping the MMA content constant. In the case of the MMA–2-EHA copolymer, the increase in molecular weight distribution with the increase in the 2-EHA content is expected, because the MMA is highly reactive and likely to be consumed faster than 2-EHA, leaving the excess of 2-EHA radicals for further polymerization. This may be the reason for the high molecular weight distribution of MMA–2-EHA copolymer. The polydispersity of the different copolymers varies from 1.8 to 3.4, which is well within the characteristic region of copolymers obtained by radical polymerization.

From the GPC data (Table III) it is evident that, intrinsic viscosity of all the copolymer systems lie in the range of 0.14 to 0.27 indicating that the copolymers have a reasonably good film forming capacity and adhesive property. The influence of $\bar{M}_n$ on the intrinsic viscosity is very well reflected in the linear relationship between $\bar{M}_n$ and intrinsic viscosity (Table III). Among the copolymer systems studied, the MBA 12 has the highest $\bar{M}_n$ and the MEHA 21 has the least value.

Solubility Behavior

After checking the solubility of freshly prepared copolymer samples in various polar and nonpolar solvents, it was observed that the copolymer samples are soluble in polar solvents such as THF, $CHCl_3$, CCl_4, toluene, ethyl acetate, DMSO, and insoluble in nonpolar solvents such as hexane, petroleum ether, methanol etc. The solubility decreases with the passage of time. This may be due to the formation of crosslinking in polymers due to inter- or intramolecular linkages. The UV radiation (from sunlight) probably abstracts hydrogen from the nearby macromolecules that finally leads to crosslinking of the polymeric chain.[18] The oxidative degradation usually leads to hardening, discoloration, and surface changes that may also be a reason for the decrease in the solubility of the copolymers.

TGA and DTA

The thermal stability of the copolymers was assessed in terms of integral procedural decomposition temperature (IPDT) value of the copolymers. IPDT values were calculated from the area under the curve[19] and were obtained within the experimental error. TGA data of the copolymers are summarized in Table IV. Thermograms of the copolymers show

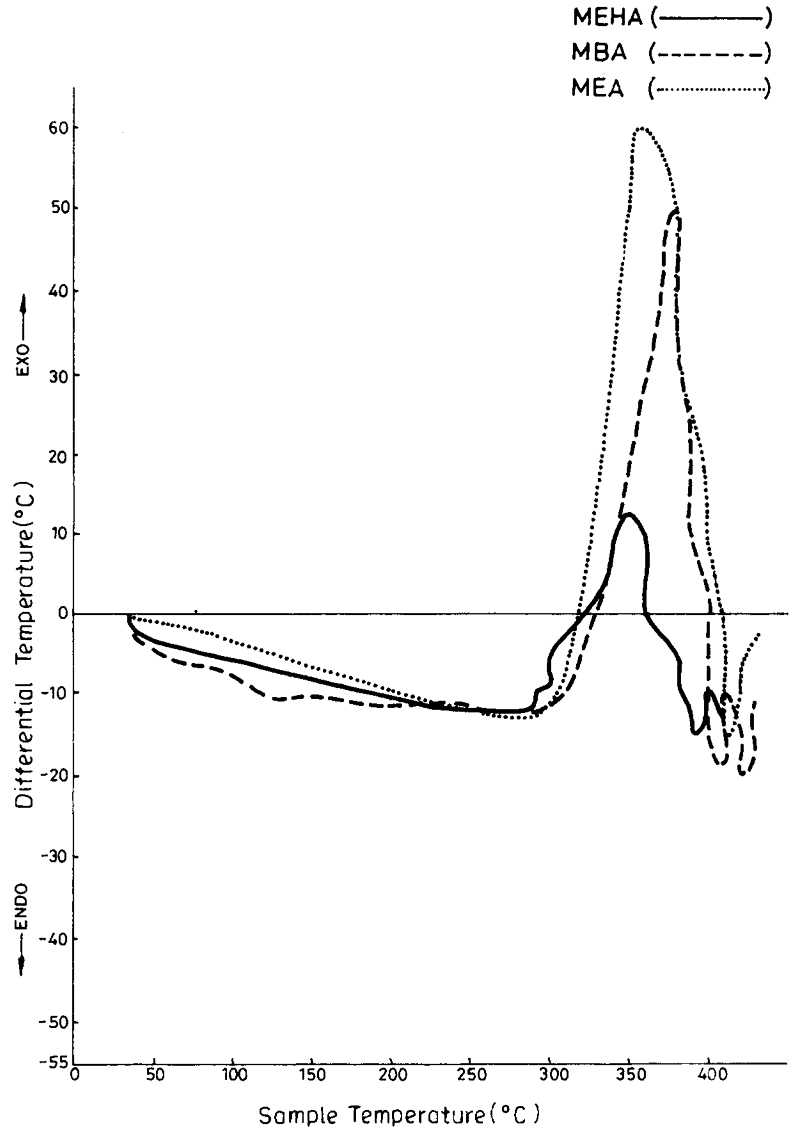

Figure 5 DTA thermograms of copolymers of methyl methacrylate with acrylate comonomers.

characteristic single stage weight loss in all the copolymer systems that may be due to the decomposition of ester linkages of the comonomers. The weight loss in each case begins in the temperature range 300–315°C and is complete around 400°C. TGA is amply supported by a single distinct exothermic peak, in the temperature range of 300–400°C on the DTA curve, in each case as expected. The initial DT (IDT), final DT (FDT), and 50% DT values were observed to be more or less the same for all copolymer systems.

From the data it is clear that the overall thermal stability of copolymers based on the only distinguishing factor, the IPDT values, is in the following order

MMA-EA > MMA-*n*-BA > MMA-2-EHA.

The overall thermal stability of the copolymers lies in the temperature range 335–370°C. It is observed that the thermal stability of the copolymer increases relatively with the increase in the MMA content of the copolymer. Among the three copolymer systems, MMA-2-EHA has the least thermal stability, that may be attributed to an increase in

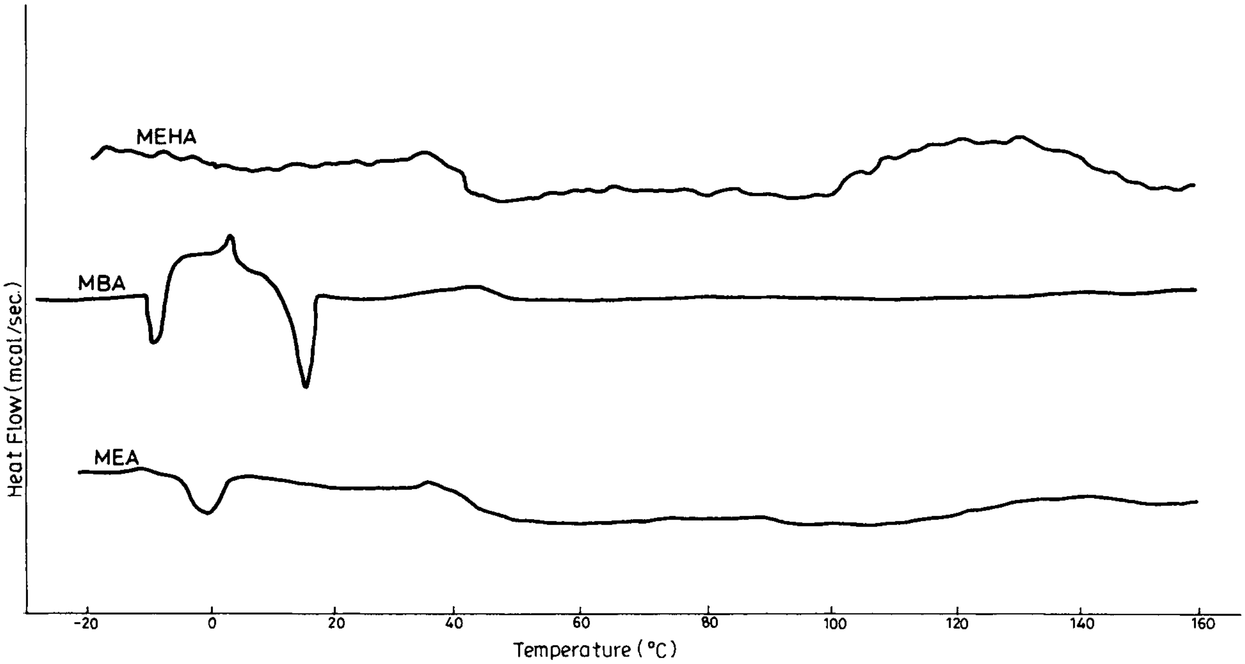

Figure 6 DSC curves of copolymers of methyl methacrylate with acrylate comonomers.

the length of the ester chain from MMA–EA through MMA-*n*-BA to MMA-2-EHA.

Glass-Transition Temperature

The reported[20] T_gs of the homopolymers and the T_gs of the various copolymer systems studied are summarized in Table V. As expected, the T_gs of the copolymers lie between the T_gs of corresponding homopolymers.[13] From Table V it is observed that the alkyl group has a significant effect on the T_gs of these polymers. In the present study, because the conversion is more than 95%, the increase in the chain length from MMA-EA to MMA-2-EHA through MMA-*n*-BA reflects in the reduction of T_g value of the copolymer system for given composition (e.g., 1 : 1) in the same order (Table V). However, in the case of MMA-2-EHA copolymer the effect of T_g value is more pronounced, probably because of the additional effect of the bulky (C_2H_5) (R′) group substitution.

The calculated T_g values of the copolymers from the Fox equation[21] are also tabulated in Table V. A comparison between the observed T_g and those calculated by the Fox equation indicates that the actual values obtained are higher than that expected theoretically in the case of the MMA–EA system. This rise in the T_g above the predicted value may be due to some specific chain stiffening effect or the possibility of hydrogen bonding between the comonomer

Table II Copolymer Composition from ^{1}H-NMR Analysis

Polymer Code	Mole Ratio in Feed	Peak Area		Conversion (%)	Mole Ratio from ^{1}H-NMR
		(—OCH_3)	(—OCH_2)		
MEA 11	1.00	0.0213	0.0119	95.1	1.19
MEA 12	0.50	0.0116	0.0134	95.4	0.50
MEA 13	2.00	0.0260	0.0076	97.1	2.28
MBA 11	1.00	0.0066	0.0039	97.7	1.1
MBA 12	0.50	0.0055	0.0058	96.5	0.63
MEHA 11	1.00	0.0079	0.0056	96.2	0.94

Table III Gel Permeation Chromatography

Polymer Code	$\bar{M}_n$ ($\times 10^{-5}$)	$\bar{M}_w$ ($\times 10^{-6}$)	$\bar{M}_z$ ($\times 10^{-6}$)	$\bar{M}_v$ ($\times 10^{-6}$)	Mol Wt Distrib.	Intrins. Viscos.
MEA 11	0.8387	0.1830	0.3100	0.1829	2.1913	0.1829
MEA 12	1.1248	0.2500	0.4479	0.2500	2.2230	0.2500
MEA 21	0.8275	0.1563	0.2509	0.1562	1.8882	0.1562
MBA 11	0.7874	0.1690	0.3002	0.1689	2.1458	0.1689
MBA 12	1.3209	0.2641	0.4932	0.2641	1.9996	0.2640
MBA 21	0.7144	0.1445	0.2390	0.1445	2.0229	0.1445
MEHA 11	0.5458	0.1708	0.3351	0.1707	3.1290	0.1707
MEHA 12	0.6797	0.2147	0.4349	0.2147	3.1593	0.2417
MEHA 13	0.7335	0.2429	0.5070	0.2428	3.3117	0.2428
MEHA 21	0.6544	0.1476	0.3498	0.1436	2.1946	0.1436
MEHA 31	0.7675	0.1481	0.2363	0.1480	1.9294	0.1480

residues,[22] but no such trend is observed in the MMA–BA and MMA-2-EHA systems.

Adhesive Properties

The results obtained from the 180° peel adhesion study of copolymers of MMA with acrylate comonomers are tabulated in Table VI. The results of the tape study reveal that with the increase in the concentration of EA or *n*-BA, adhesive strength increases. On the other hand the hardness of the material increases at the cost of its adhesive strength when the concentration of MMA is increased, which may be due to the selective incorporation of MMA in the copolymer chain. Nevertheless, MMA served as the strengthening factor of the copolymers. In the case of the MMA–2-EHA system the adhesive strength decreases abruptly with an increase in the 2-EHA or MMA content, keeping the other comonomer content constant. 2-EHA being highly tacky and soft with its increase in the concentration of the copolymer the cohesive strength decreases and hence the adhesive strength drops down. Whereas with the increase in the MMA concentration in the copolymer the cohesive strength crosses the optimum level thus increasing the hardness and in the process adversely affecting the adhesive strength. However, the optimum peel adhesion is observed for a copolymer of MMA with 2-EHA at 1 : 1 molar ratio.

Table IV Thermal Properties of Copolymers of MMA and Acrylate Comonomers

Polymer Code	IDT (°C)	50% DT (°C)	FDT (°C)	IPDT (°C)
MEA 11	307.5	382.0	405.0	352.1
MEA 21	310.0	378.0	405.0	366.9
MBA 11	315.0	378.0	403.0	345.4
MBA 21	312.5	385.0	410.0	358.9
MEHA 11	307.5	375.0	408.0	337.9
MEHA 31	302.0	345.0	385.0	350.9

IDT, initial decomposition temperature; DT, decomposition temperature; FDT, final decomposition temperature; IPDT, integral procedural decomposition temperature.

Table V Glass-Transition Temperatures

Polymer Code	T_g Homopolymers	T_g Copolymers	T_g Calculated fr. Fox Eq.
PMMA	105	—	
MEA 11	—	51.0	28.68
MEA 12	—	39.5	9.33
MEA 21	—	68.0	50.94
PEA	−22	—	—
MBA 11	—	18.5	4.77
MBA 12	—	10.0	−16.59
MBA 21	—	26.0	39.50
PBA	−54	—	—
MEHA 11	—	10.0	−16.59
MEHA 31	—	22.0	30.03
PEHA	−85	—	—

Fox equation:

$$\frac{1}{T_g\ (\text{copolymer})} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}}$$

where, W_1 is the weight fraction of component 1 and T_{g_1} is the T_g of the homopolymer of component 1.

Table VI Adhesive Strength of Copolymers of MMA with Acrylate Comonomers

Polymer Code	Adhes. Strength (g)
MEA 11	1080
MEA 12	1350
MEA 13	1845
MEA 21	475
MEA 31	286
MBA 11	1092
MBA 12	1495
MBA 13	1550
MBA 21	1000
MBA 31	565
MEHA 11	1435
MEHA 12	895
MEHA 13	300
MEHA 21	955
MEHA 31	317

As the copolymerization has been carried out at more than 95% conversion, the order of the adhesive strength for the three systems studied appears to be:

$$\text{MMA-EA} > \text{MMA-}n\text{-BA} > \text{MMA-2-EHA},$$

in consonance with the reactivity of the individual comonomers.

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