Copolymers of Higher Alkyl Methacrylates with Triallyl Cyanurate

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SYNOPSIS

Copolymers of higher methacrylates (propyl, pentyl, hexyl, cyclohexyl, heptyl, octyl, and dodecyl) with triallyl cyanurate were synthesized by free-radical polymerization using benzoyl peroxide as initiator. The properties of the copolymers such as thermal stability, T_g, Vicat softening temperature, hardness, refractive indices n_D, chemical stability, density, and shrinkage on polymerization were studied. The influence of the alcohol alkyl chain length in methacrylates and the content triallyl cyanurate in copolymers on their properties is discussed. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Although the properties of alkyl methacrylate polymers, particularly those of poly(methyl methacrylate) have been widely reported in the scientific and technical literature,[1-8] only few references can be found on the properties of higher poly(alkyl methacrylates) and their copolymers.

The present study reports on a number of polymeric higher methacrylic (MA) esters [i.e., propyl (Pr), pentyl (Pt), hexyl (Hx), cyclohexyl (CHx), heptyl (Hp), octyl (Oc), and dodecyl (Dd)] and theirs copolymers with triallyl cyanurate (TAC).

Triallyl cyanurate [2,4,6-tris(allyloxy)-s-triazine] monomer[9] is commercially important as crosslinking agent in curing processes.[10] It has also been used as a crosslinking agent for unsaturated resin. The use of triallyl cyanurate in the copolymerization with alkyl methacrylates provides a possibility of synthesis of copolymers with high thermal stability.[11-15] The studies were undertaken in order to obtain information on the influence of the length of alcohol alkyl chain in methacrylate and of the content of triallyl cyanurate on properties of the copolymers.

The copolymers—PrMA–TAC, PtMA–TAC, HxMA–TAC, CHxMA–TAC, HpMA–TAC, OcMA–TAC, and DdMA–TAC—were obtained by free-radical polymerization carried out in bulk using benzoyl peroxide as initiator. Each copolymer contained about 5, 10, 15, and 20 wt % of TAC. Attempts have been made to explain differences in properties of copolymers that are caused by the presence of branching introducing triallyl cyanurate units.

EXPERIMENTAL

Monomers

The monomeric esters of methacrylic acid—propyl (PrMA), pentyl (PtMA), hexyl (HxMA), cyclohexyl (CHxMA), heptyl (HpMA), octyl (OcMA), and dodecyl (DdMA)—were prepared by transesterification from methyl methacrylate and corresponding alcohols, as described elsewhere.[16-18] The structure and purity of monomers were checked by measuring their physical properties (see Table I) and by IR and ^{1}H-NMR analyzes.[19]

The synthesis of TAC was described elsewhere.[20] The nitrogen content was 16.8% as determined by Kieldahl's[21] method (calculated 16.8%), mp 300–301 K, bp 419–413 K, $n_D^{20} = 1.5060$, $n_D^{25} = 1.5049$.

Benzoyl peroxide (BP), pure grade (Argon, Łódź, Poland), contained 86.5% of BP as analyzed according to Ref. 22.

Copolymerization

PrMA–TAC, PtMA–TAC, HxMA–TAC, CHxMA–TAC, HPMA–TAC, OcMA–TAC, and DdMA–TAC

Table I   Physical Properties of Alkyl Methacrylates

Monomer	Bp (K)/10^2 N/m^2	Yield (%)	d_4 (g/cm^3)	n_D^{2o}	Molecular Weight Calcd.	Molecular Weight Found[a]	Saponification Number Calcd.	Saponification Number Found
PrMA	313/10.7	50	0.9060	1.4191	128.2	128.6	438	444
PtMA	350/28.7	60	0.8913	1.4277	156.0	154.0	359	362
HxMA	374/32.0	75	0.8833	1.4300	170.3	171.6	329	333
CHxMA	345/5.3	74	0.9680	1.4581	168.2	176.9	333	332
HpMA	335/5.3	60	0.8825	1.4322	184.3	182.9	304	305
OcMA	393/21.3	75	0.8830	1.4378	198.3	196.1	283	282
DdMA	452/18.7	68	0.8753	1.4450	254.4	222.2	221	219

[a] Cryoscopic measurements in dioxane.

copolymers were obtained by free-radical copolymerization using 0.2 wt % BP as the initiator. Respective homopolymers were obtained for reference at the same conditions. Compositions of copolymers are presented in Table II. The bulk copolymerizations were carried out in 20 cm^3 glass ampules which were heated in a thermostat according to the following temperature–time procedure, starting at 310 K. After every 6 h the temperature was raised by 10 K up to 353 K. Then the ampules were transferred to an oven and further heated to obtain crosslinked copolymers.

Measurements

Infrared spectra of copolymers (KBr pellets) were recorded on a SPECORD-71 IR spectrometer (Carl Zeiss, Germany).

^{1}H-NMR (CDCl$_3$) spectra were recorded on BS 587 A spectrometer (Czechoslovakia) at the frequency of 80 MHz. Elemental analysis was carried out using EA 1108 Elemental Analyzer (Carlo Erba, Italy).

Table II   Composition of Starting Mixtures of Alkyl Methacrylates and Triallyl Cyanurate Comonomers

Sample No.	Alkyl Methacrylate (wt %)	Triallyl Cyanurate (wt %)
I	100	0
II	0	100
III	95	5
IV	90	10
V	85	15
VI	80	20

Copolymer Properties

Thermal Strength

Thermal studies were carried out on an OD-102 derivatograph (Hungary) for powdered homo- and copolymers containing ca. 10 and 20 wt % of TAC. The measurements were made in the temperature range 293–1273 K at heating rate of 10 K/min in an inert (argon) and in an oxidizing (air) atmosphere, with sample weight of 20–50 mg. Sensitivity of DTA-1/20; sensitivity of DTG-1/10. Thermal studies were also carried out by using Madorsky method[23] for the homo- and copolymers containing ca. 5, 10, 15, and 20 wt % of TAC in the temperature range 373–623 K, in air as oxidizing atmosphere, with sample weight 20–50 mg.

Glass Transition Temperature (T_g)

The measurements of T_g were carried out on a DSC-1B Perkin-Elmer scanning microcalorymeter (USA) for homo- and copolymers containing ca. 10 and 20 wt % of TAC. Before every measurement the sample was cooled down from 420 to 233 K. Experiments were carried out on about 16-mg samples under air and nitrogen at a flow rate 30 mL/min, at the heating rate of 16, 32, and 64 K/min and at the cooling rate 4 K/min. Sensitivity was 8 mcal/s.

Vicat Softening Temperature

This was measured by the Vicat test using Rδ Ceast-Torino apparatus (Italy). The measurements were carried out for copolymers in the form of disk (diameter: ca. 30 mm, thickness: ca. 5 mm) with the load of 49 N and heating rate of 50 K/h.

Table III   Results of Elemental Analysis of Alkyl Methacrylate with Triallyl Cyanurate Copolymers[a]

Copolymer	Sample No.	N[b] (%)	C[b] (%)	H₂[b] (%)
PrMA + TAC	IV	1.787	61.670	9.123
	VI	3.491	64.010	8.794
PtMA + TAC	IV	1.665	51.310	9.483
	VI	3.494	61.681	9.547
HxMA + TAC	IV	2.054	58.301	9.359
	VI	3.461	59.064	9.189
CHxMA + TAC	IV	2.158	66.231	8.376
	VI	4.187	70.369	8.404
HpMA + TAC	IV	2.127	67.995	10.363
	VI	3.747	64.397	9.915
OcMA + TAC	IV	1.712	70.040	10.750
	VI	3.752	70.762	10.115
DdMA + TAC	IV	1.957	69.192	11.272
	VI	3.385	71.192	10.806

[a] Composition of copolymers is presented in Table II.
[b] Average values from the two disignates.

Brinnell Hardness

The measurements were made using a Brinnell tester (HPK 746, Feinmechanik, Ralf Kögel, Germany) for homo- and copolymers of PrMA–TAC and CHxMA–TAC containing ca. 10 and 20 wt % of TAC, respectively. The samples were in the form of disks (diameter: ca. 30 mm. and thickness ca. 5 mm). The hardness was calculated using the formula $H_k = F/d\pi h$ (N/m²), where F is the load (kG), d is the diameter of penetrating ball (m × 10⁻³), and h is the depth of penetration (m × 10⁻³).

Refractive Indices $n_D{}^{20}$

The refractive indices of the homo- and copolymers in the form of sheets (thickness from 2 to 3 mm) were measured at 293 K by microscopy method. The refractive indices were calculated from the formula $n_D{}^{20} = d/h$ where d is the thickness of sheet (mm) measured by a micrometer at 293 K and h is the thickness of sheet (mm) measured by the microscope at 293 K. Three measurements were made for each sheet.

Chemical Resistance

Chemical resistance of the homo- and copolymers was studied according to a standard procedure.[24] The following organic solvents, inorganic acids, and alkali were used: acetone, benzene, 1,4-dioxane, methanol, chloroform, acetic acid, hydrochloric acid aq., nitric acid, sulfuric acid (concentrated or diluted aqueous solutions), and sodium hydroxide (10%, 40% aq. sol.). Samples of the copolymers were immersed in each agents for 7 days.

Density and Shrinkage on Polymerization

The density of homo- and copolymers was measured at 293 K using a hydrostatic balance and ZnCl₂–water mixture, and the density of the comonomers with pycnometer at 293 K. Two measurements were made for each copolymer. The shrinkage (Sh) of the comonomer on copolymerization was calculated from the following formula[1]: $Sh = (d_{cp} - d_{cm})/d_{cp} \times 100\%$, where d_{cp} is the density of copolymer and
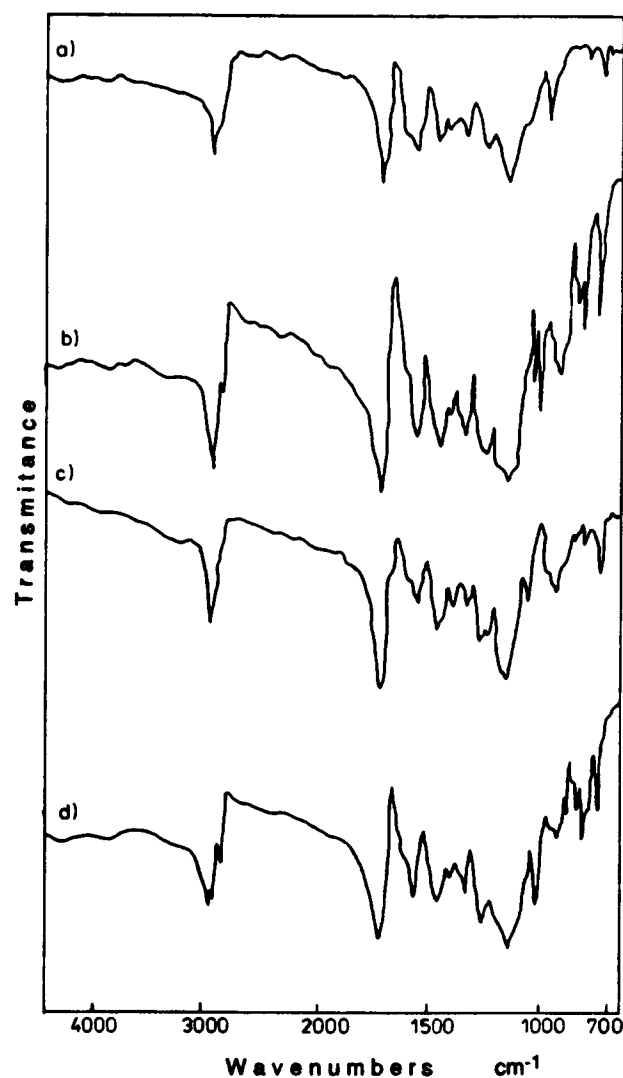
Figure 1   Infrared spectra for some copolymers: (a) PrMA–TAC, (b) PtMA–TAC, (c) CHxMA–TAC, (d) OcMA–TAC (content of TAC 10 wt %).

Table IV T_{dt}, T_{d50}, T_{max} for Homo- and Copolymers of Alkyl Methacrylates with Triallyl Cyanurate Determined by Dynamic Method in Argon and by Static Method in Air[a]

| Homo- and Copolymer	Sample No.	T_{dt} (K)	T_{d50} (K)	T_{max} (K)	T_{d50} (K)[a]
PrMA + TAC	I	493	553	583	515
	II	563	693	713	578
	III	—	—	—	539
	IV	513	613	643	547
	V	—	—	—	555
	VI	523	643	703	563
PtMA + TAC	I	468	563	593	508
	III	—	—	—	531
	IV	483	593	663	543
	V	—	—	—	551
	VI	488	623	683	559
HxMA + TAC	I	463	558	573	535
	III	—	—	—	553
	IV	483	593	643	563
	V	—	—	—	566
	VI	488	623	663	576
CHxMA + TAC	I	463	543	623	531
	III	—	—	—	543
	IV	478	613	673	551
	V	—	—	—	556
	VI	483	633	683	561
HpMA + TAC	I	483	568	593	536
	III	—	—	—	548
	IV	493	626	653	551
	V	—	—	—	556
	VI	498	648	663	561
OcMA + TAC	I	483	573	593	538
	III	—	—	—	552
	IV	483	573	593	561
	V	—	—	—	565
	VI	503	633	653	571
DdMA + TAC	I	498	573	593	545
	III	—	—	—	556
	IV	492	643	573	561
	V	—	—	—	565
	VI	510	673	693	572

[a] Composition of copolymers is presented in Table II.

d_{cm} is the density of comonomer, both at 293 K (g/cm^3).

RESULTS AND DISCUSSION

The compositions of polymerization mixture of PrMA-TAC, PtMA-TAC, HxMA-TAC, CHxMA-TAC, HpMA-TAC, OcMA-TAC, and DdMA-TAC are shown in Table II. All homo- and copolymers were obtained by bulk radical polymerization of the corresponding monomers using 0.2 wt % of benzoyl peroxide as an initiator. The polymerization was carried out long enough and at sufficiently high temperature to convert comonomers to crosslinked resins. The compositions of copolymers were verified by elemental and IR analyses. The results of elemental analysis are shown in Table III. The IR spectra for some copolymers are shown in Figure 1. In all IR spectra intense absorption bands for methacrylates (homopolymers) are in the range of 1730 cm^{-1} (C=O), 1175 cm^{-1} ($\langle$C—O—C$\rangle$), 1070–1040 cm^{-1} and 720 cm^{-1} ($\langle$C—(C—C)n—), and for the -triazines (copolymers) in range 1575 cm^{-1} ($\langle$C=N— in the ring), 1415–825 cm^{-1} (for the s-triazine ring). No absorption band for C=C double
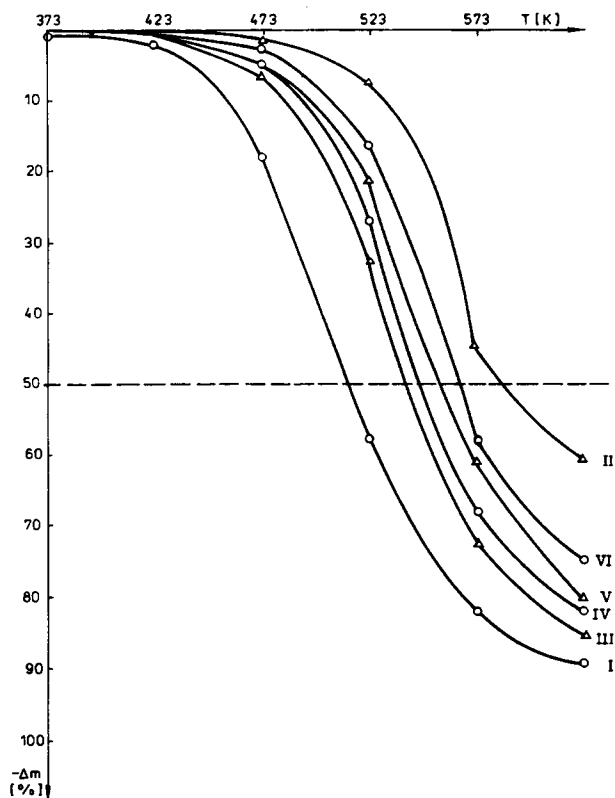
Figure 2 The weight loss plots for homo- and copolymers of PrMA–TAC. (I) polymethacrylates, (II) poly(triallyl cyanurate). Content of TAC: (III) 5 wt %, (IV) 10 wt %, (V) 15 wt %, (VI) 20 wt %.

bond in the range 1640–1660 cm^{-1} was observed. The homo- and copolymers of PrMA–TAC and CHxMA–TAC were in the form of solid, hard, and transparent resin. The remaining samples were not transparent and had the form of elastic resins of different hardness. Poly(triallyl cyanurate) was hard, brittle, and transparent resin of a light-green color.

The thermal analysis of the homo- and copolymers were conducted by dynamic and static methods. Thermal stability for all copolymers containing ca. 10 and 20 wt % of TAC was studied by a dynamic method using OD-102 derivatograph in an inert (argon) atmosphere. The thermal stability was taken to be the temperatures of initial (5%) weight loss of the sample (T_{di}), the temperature of 50% weight loss of the sample (T_{d50}) and the temperature of maximum decomposition rate (T_{max}). The results are presented in Table IV. The temperature of maximum rate of copolymer degradation corresponded to the temperature at which maxima on differential thermal gravimetry (DTG) curves appeared. The maximum weight loss and minimum temperature of

5% (T_{di}) and 50% decomposition (T_{d50}) were observed for homopolymers. The analysis of DTG curves for the copolymers indicated that the temperatures of maximum decomposition rate (T_{max}), were shifted toward the higher temperature region. Other, less intense peaks of the thermal degradation process were also observed on DTG curves. The length and structure of alkyl group in methacrylates exert a certain influence on the thermal stability of homo- and copolymers. The values T_{di}, T_{d50}, and T_{max} slightly decreased as the size of alkyl group in the methacrylates increased (Table IV).

Thermal effects occurring upon heating the samples were also observed on differential thermal analysis (DTA) curves. For poly(methacrylates) an endothermal process of depolymerization and evaporation occurred at about 523–583 K. For the copolymers, the endothermal changes appeared in somewhat higher temperature range at about 633–683 K depending on the kind of methacrylate used and on the content of TAC in copolymer. It can be deduced from reactivity ratios that triallyl cyanurate does not readily copolymerize with reactive mono-
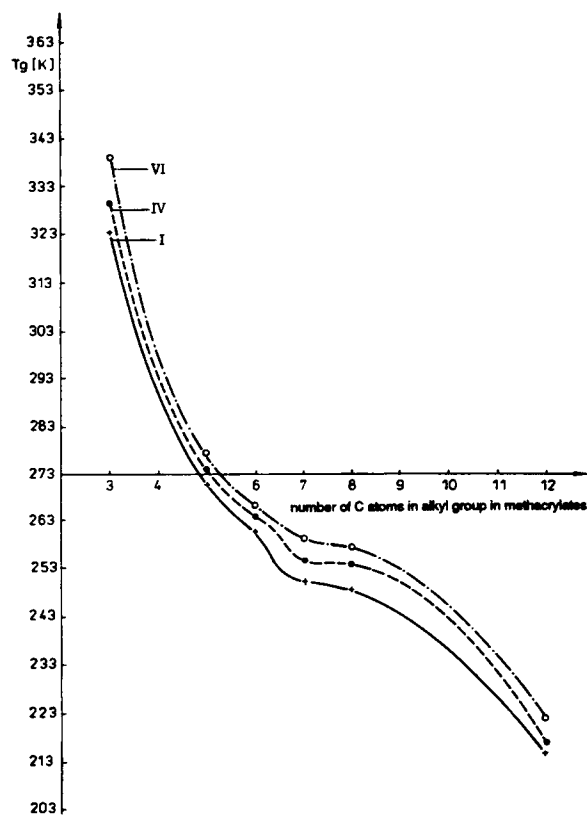
Figure 3 The T_g values vs. the number of C atoms in alkyl group in methacrylates: (I) polymethacrylates, (II) copolymers with 10 wt % of TAC, (III) copolymers with 20 wt % of TAC.

Table V   Some Physical Properties of Homo- and Copolymers of Alkyl Methacrylates and Triallyl Cyanurate[a]

| Sample No.	PrMA–TAC			CHxMA–TAC		
	Brinell 10^4 (N/m^2)	Vicat (K)	n_D^{2o}	Brinell 10^4 (N/m^2)	Vicat (K)	n_D^{2o}
I	3952	333	1.4800	10562	353	1.5100
II	12088	419	—	12088	423	1.5000
III	5080	338	1.4600	10797	358	1.5000
IV	5227	340	1.4400	11523	361	1.5000
V	5540	342	1.4100	11572	362	1.4800
VI	5786	346	1.4000	11964	367	1.4600

[a] Compositions of copolymers are presented in Table II.

mers,[25] including alkyl methacrylates,[19] but if polymerization is forced to completion, the cured products are mixtures of copolymers and homopolymers.

For the copolymers the exothermal changes on DTA curves were probably a result of various chemical transformations. Thermal studies of the copolymers were also conducted by using a static (Madorsky) method.[23] Two series of measurements were carried out for the homo- and copolymers containing ca. 5, 10, 15, and 20 wt % of TAC. The weight losses of homopolymers and copolymers of PrMA–TAC heated for 45 min at the temperature range from 373 to 673 K in air are shown in Figure 2. The thermal stability was taken to be the temperature of 50% weight loss of the sample (T_{d50}). These values

varied considerably with copolymer composition. The maximum value of weight loss and the minimum temperature of 50% decomposition (T_{d50}) were observed for homopolymers. The increase in TAC content in copolymers caused a rise of T_{d50} values, while the weight loss decreased. The data is shown in Table VI. The values of T_{d50} obtained by both dynamic and static methods seem to confirm the improvement thermal stability effect of the presence of TAC units. As low as 10 wt % content of TAC in the copolymers raises the T_{d50} value by about 30–50 K as measured by static method, and even by about 70 K, as measured by dynamic one.

The presence of TAC units in copolymers with alkyl methacrylates causes an increase in their glass transition temperature, as measured by Vicat's
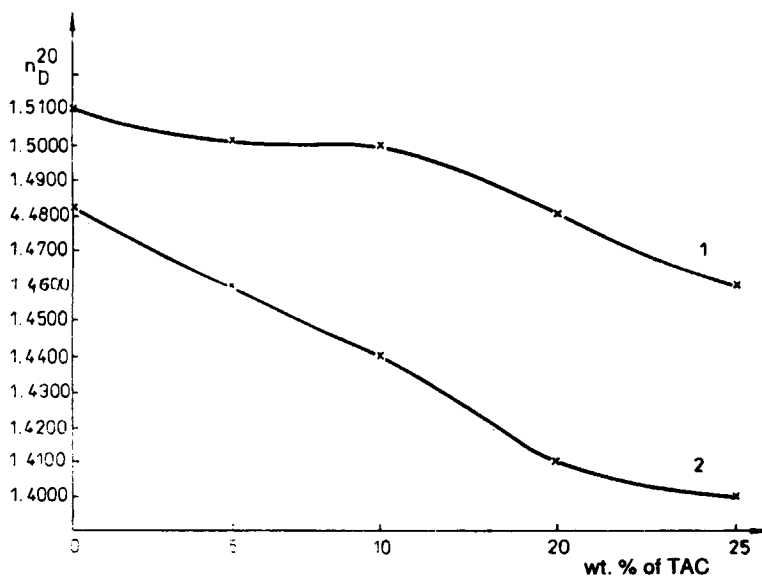
Figure 4   The plots of n_D^{20} vs. TAC content in the copolymers: (1) homo- and copolymers of CHxMA–TAC and (2) homo- and copolymers of PrMA–TAC.

**Table VI   Shrinkage of Polymerization (%) of Homo- and Copolymers of Alkyl
Methacrylate and Triallyl Cyanurate[a]**

Sample No.	S_h (%)						
	PrMA–TAC	PtMA–TAC	HxMA–TAC	CHxMA–TAC	HpMA–TAC	OcMA–TAC	DdMA–TAC
I	16.9	15.9	13.1	12.9	11.8	11.1	6.8
III	17.1	15.8	13.3	12.9	11.7	10.3	8.1
IV	16.3	15.6	13.1	13.0	12.0	10.2	8.7
V	16.0	15.6	13.5	13.3	11.5	9.4	9.2
VI	16.3	15.4	13.2	13.2	12.8	10.2	8.7
II	10.8	—	—	—	—	—	—

[a] Composition of copolymers is presented in Table II.

method. The T_g of homo- and copolymers containing 10 and 20 wt % of TAC was also measured using differential scanning calorimetry (DSC) in air and nitrogen atmosphere. The average values of glass transition temperature were extrapolated to zero heating rate according to Strella's method.[26] The relationships of T_g of homo- and copolymers for both compositions (10 and 20 wt %) versus the number of C atoms in alkyl group of methacrylate are plotted in Figure 3. It can be seen from this figure, that T_g increases with TAC content in the copolymers and decreases as the alkyl group in methacrylate becomes longer.

The measurements of Vicat softening temperature and Brinnell hardness were conducted for homo- and copolymers of PrMA–TAC and CHxMA–TAC, only. The remaining homo- and copolymers were above T_g at room temperature. The average values from three (Vicat), and from seven measurements (Brinnell), are presented in Table V. An effect of large group in CHxMA on both Vicat and Brinnell hardness can clearly be seen. The values of refractive indices n_D^{20} for the same homo- and copolymers are also presented in Table V. The plot of n_D^{20} homo- and copolymers vs. TAC content in the copolymers is shown in Figure 4.

The chemical resistance of homo- and copolymers against some organic solvents, inorganic acids, and alkalies were studied. In general the samples of homo- and copolymers are resistant against 10% aqueous solutions of hydrochloric acid, nitric acid, sulfuric acid, and 10 and 40% aqueous solutions of sodium hydroxide. In other solvents and chemicals they either dissolve or swell. Some of them get clouded. Poly(triallyl cyanurate) was insoluble in solvents such as chloroform and acetic acid.

The results of shrinkage on polymerization for all homo- and copolymers are summarized in Table VI.

CONCLUSIONS

Modification of higher alkyl methacrylate polymers by triallyl cyanurate units (5–20 wt %) produced copolymers having better thermal stability and some physical properties improved (e.g., chemical resistance, Brinnell hardness, Vicat temperature) compared to unmodified alkyl methacrylate polymers. It has been found that polymerization shrinkage becomes smaller the longer the alkyl group is in methacrylate.

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