Synthesis, Crosslinking, and Abrasion and Weathering Properties of (Meth)Acrylate-Terminated Bisphenol A Polycarbonates

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ABSTRACT: (Meth)acrylate terminated bisphenol A polycarbonates [(M)AC PCs] were prepared under interfacial conditions by reaction of (meth)acryloyl chloride with bisphenol A (BA) followed by phosgenation. Addition of (M)ACl to an interfacial mixture of BA containing a catalytic amount of triethylamine followed by phosgenation gave linear polymers with good control of molecular weight. Thermal crosslinking of MAC PCs was generally achieved only in the presence of dicumyl peroxide. Between 75 and 98% gel was obtained by using 2 wt % initiator and heating for 30 min each at 150 and 200°C. All of the AC PCs crosslinked without added initiator to form 92–100% gel by heating for 30 min at 250°C. Coatings of high crosslink density (M)AC PCs on linear BA PC plaques were prepared by a combination of solvent casting, compression molding, and (optionally) oven curing. Moderate to high crosslink density (M)AC PC coatings showed relatively high pencil hardness values and good abrasion resistance. In weathering studies, both MAC and AC PC-coated plaques showed low YI increases, but the MAC PC coating developed higher haze due to microcracking. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 663–675, 1999

Key words: polycarbonate; acrylate; methacrylate; terminator; crosslinking; hardness; abrasion resistance; weathering

INTRODUCTION

Bisphenol A polycarbonates (BA PCs) having thermally reactive end groups are the basis of a host of potential new polymeric materials having a wide range of improved properties compared to standard BA PCs, such as solvent resistance, ignition resistance, surface hardness, and melt processability. These improved properties, previously unrealized in BA PCs alone, were first demonstrated by thermosets[1] and thermoplastic alloys[2] of benzocyclobutene (BCB)-terminated BA PCs, and result from the unique molecular architecture they produce. The high crosslink density versions of BCB PCs can be coated or laminated onto BA PC to provide high measures of abrasion resistance.[3] Given these results and the considerable recent work on the thermal[4] and photochemical[5] crosslinking of (meth)acrylate terminated compounds, the extension of these studies to the titled polymers was of keen interest.

Several types of (meth)acrylate-terminated PCs have been previously reported. High molecular weight MAC BA PCs are known to partially crosslink upon exposure to UV radiation in the presence of photoinitiators.[6,7] Dissolution of the soluble fraction from these partially crosslinked PCs provides shaped articles useful as membranes.[8] High molecular weight MAC-terminated copolycarbonates derived from BA and 4,4′-dihy-

droxybenzophenone, a comonomer that serves as a photoinitiator, are also crosslinked by UV.[9] A process to obtain modified thermoplastic PCs by treating granulated, high molecular weight alkenyl-substituted PCs, exemplified by MAC BA PC, with a radiation-to-surface crosslink and then extrude or mold has been claimed.[10] Branched PCs at least partially terminated with AC groups show improved solvent resistance after UV exposure.[11] Many types of (meth)acrylate terminated aliphatic PCs are also known, and are generally used in coating applications.[12] The degradation of crosslinked methacrylate terminated aliphatic PCs has been studied.[13, 14] Interestingly, in these earlier works only relatively high molecular weight ($M_w > 10,000$) aromatic AC or MAC PCs have been examined.

In this study, the interfacial synthesis and crosslinking of acrylate (AC, R = H) and methacrylate (MAC, R = CH$_3$) terminated BA PCs (**1**) were investigated to expand our understanding of the structure–property relationships of this class of polymers, and the abrasion resistance and weathering of these new thermosets based on linear BA PC were evaluated.

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EXPERIMENTAL

Chemicals

Bisphenol A (BA, PARABIS™ grade), dichloromethane (technical grade), and BA PC (CALIBRE™ 300-15 grade) were used as received from The Dow Chemical Company. Aqueous sodium hydroxide (50 wt %) (caustic, Fisher Scientific), triethylamine (TEA, Aldrich Chemical Co.), methacryloyl chloride (MACl, Aldrich Chemical Co.), acryloyl chloride (ACl, Aldrich Chemical Co.), phosgene (5-lb. cylinders from Matheson Gas Products), dicumylperoxide (DCP, Aldrich Chemical Co.), 1,1′-azobis(cyanocyclohexane) (VAZO 88, DuPont Chemicals), 2,6-di-t-butyl-4-methylphenol (BHT, Aldrich Chemical Co.), were obtained from the indicated suppliers and used as received.

Analyses

Gel permeation chromatography (GPC) and reversed-phase liquid chromatography (LC) were

done as previously described.[1] Gel content was determined by submersing the crosslinked material in dichloromethane for 18 h at room temperature, collection of the insoluble fraction with suction, and evaporation of the retained solvent in a 100°C vacuum oven for 18 h.

Synthesis

Preparations of AC and MAC PCs were done using batch[1] or microscale[15] equipment as previously reported. Two interfacial process variations were employed, with the relative molar amount of (M)ACl/BA expressed as mol/mol or "m/m." In the first variation, (M)ACl was added to mixtures of BA, aq. NaOH, and dichloromethane, and then phosgenated and coupled using catalytic amounts of TEA.[1] In the second variation, TEA is present during the addition of (M)ACl (as described below). High molecular weight AC and MAC PCs were recovered by hot-water devolatilization.[1] Dichloromethane solutions of low molecular weight polymers ($M_w < 5,000$) were either precipitated into 4 vol of heptane and solvent stripped to a dry powder or evaporated to form films.

Synthesis of 0.10 m/m AC PC (Process 2)

To a nitrogen purged 2 l resin kettle fitted as previously described[1] was added 85.0 g (0.3723 mol) BA, 5 mL (3.5 g, 0.0347 mol) TEA, 460 mL water, and 230 mL dichloromethane. With stirring, 3.15 mL (3.37 g, 0.0372 mol) ACl was added dropwise along with 50% aqueous sodium hydroxide to maintain an aqueous phase pH of 9. After 15 min of stirring 39 g (0.395 mol, 80% of total) phosgene was added at about 1 g/min. with addition of sodium hydroxide to maintain the above pH. Then 438 mL dichloromethane was added and the pH set point was increased to 11, after which 10 g (0.10 mol, 20% of total) phosgene was added with stirring. The pH of the mixture was reduced to about 9 with addition of 6 g of phosgene to complete the polymerization. The polymer solution was washed with 1 N HCl and with water, and the polymer was then isolated by addition of the solution to ~90°C water with stirring.

Other (M)AC PCs were prepared by this process using adjusted amounts of (M)ACl as indicated in the text.

Crosslinking

Crosslinking was done by placing ~1-g quantities of polymer (optionally filmed from dichlorometh-

ane solutions containing additives as noted in the text) in aluminum dishes into a N_2 purged oven at the times and temperatures noted in the text.

Coatings on BA PC

A coating of 1.0 m/m MAC PC was applied to 15 MFR BA PC substrates by applying a 27 wt % solution of the linear polymer onto a 0.002″-thick Al sheet (to cover an area as described below and using two times the amount needed to fill the coating mold) with a syringe. The solvent was evaporated in a fume hood using a heat lamp for 2 h, then in a vacuum oven at ~120°C and ~30″ vacuum for 1 h. The foil holding the polymer was placed onto a compression molded BA PC plaque retained in its mold separated by a coating mold made from two thicknesses of Al sheet cut to the same length and width dimensions as the plaque mold. The materials were compression molded under N_2 for 5 min at 140°C and 40 kpsi, then for 5 min at 150°C and 40 kpsi. The mold assembly was then placed in a 200°C oven with a N_2 purge for 1 h, and then compression molded again at 200°C and 40 kpsi for 5 min.

AC PC coatings were prepared as described above except that only compression molding under N_2 was done at 250°C and 40 kpsi for 20 min, then at 270°C and 40 kpsi for 1 min, then cooled to 100°C and 40 kpsi.

Coated plaques with dimensions of 1.5 × 3 × 1/8″ and of 5.5 × 5.5 × 1/16″ were cut for weathering studies and abrasion resistance testing, respectively.

Physical Testing

Pencil hardness evaluations were conducted according to ASTM D-3363 using a HA-H501 Pencil Hardness Gage, produced by the Paul N. Gardner Company, Inc. Abrasion resistance evaluations were conducted according to ASTM D1044-85 using a Taber Model 5150 Abraser. A 500-g load was placed on each CS-10F grade wheel. Crosspolarization with reflected light was used on an Olympus Vanox-S AH-2 microscope to differentiate the coating from the substrate and to measure the thickness of the coating.

Accelerated weathering was performed in an Atlas model Ci65A xenon arc weatherometer. The xenon lamp was fitted with borosilicate inner and outer filters. The instrument was operated under the following conditions according to ASTM D-2565: 102 min light spray, 18 min light plus water spray per every 2-h period; 63°C black panel temperature; 50% relative humidity; 0.35 W/m^2 irradiance at 340 nm. All coated samples were backed with aluminum panels to prevent light penetration through the uncoated backside of the sample.

Yellowness index (YI) and % haze were quantified using a HunterLab ColorQuest Sphere Spectrocolorimeter. Readings were taken using large area view, illuminant D_{65}, 2° observer angle, and XYZ coordinates. YI measurements conform to ASTM D1925. An Olympus model BH-2 microscope was used to observe microcracking in weathered (M)AC PC-coated samples.

RESULTS AND DISCUSSION

Synthesis of MAC PCs

The synthesis of (M)AC PCs under interfacial reaction conditions was investigated because of the preponderant use of this process type in the manufacture of aromatic PCs. A high molecular weight MAC PC was prepared using process variation 1, in which BA disodium salt was allowed to react with MACl (0.06 m/m) under interfacial conditions prior to phosgenation (Scheme 1). The intermediate products are presumed to be predominantly BA monomethacrylate **2a**, and a minor amount of BA dimethacrylate **3a**. Phosgenation at high pH and subsequent TEA catalyzed coupling gave 0.06 m/m MAC PC having the expected molecular weight distribution (Table I). GPC analysis shows a monodisperse peak having a small amount of a low molecular weight component (Fig. 1). LC analysis shows this product to consist of the expected distribution of linear methacrylate terminated and cyclic BA oligocarbonates (Fig. 2), except for the relatively high concentration of an early eluting compound having a retention time (5.4 min) corresponding to that of BA dimethacrylate. The UV spectra of the linear methacrylate terminated oligomers have UV maxima < 250 nm and show an increasing absorbance at 265 nm as the oligomer degree of polymerization (which is proportional to retention time), and hence, carbonate content, increases (spectra 1, 2, and 4, Fig. 2). BA cyclic oligocarbonates have UV maxima near 265 nm (spectrum 3, Fig. 2). The polymer peak at ~50 min retention time in the LC is narrow, indicative of a completely coupled, high molecular weight polymer.

Scheme 1   Synthesis of (M)AC PCs by standard interfacial process.

A 1.0 m/m MAC PC prepared by this standard process has a bimodal distribution as shown by GPC (Fig. 3) due to the formation of a high concentration of BA dimethacrylate and a resultant high molecular weight (Table 1). LC analysis shows the predominant early eluting peak and the presence of relatively small amounts of higher oligomers (Fig. 4). This result contrasts with those of low molecular weight PCs terminated by phenols, which usually show a series of oligomers, starting from the phenol-derived monocarbonate, in gradually decreasing concentrations.[1]

A much narrower molecular weight distribution in 1.0 m/m and other relatively low molecular

Table I   Molecular Weight Distributions from GPC Analysis of (M)AC PC's

Terminator	m/m	Process	M_n	M_w	M_z	Disp.
MACI	0.06	1	7447	19,583	30,817	2.63
MACI	1.00	1	1330	3102	71,489	2.33
MACI	1.00	2	488	878	1565	1.80
MACI	0.70	2	606	1686	5377	2.79
MACI	0.50	2	729	2529	5618	3.47
ACI	0.10	1	1852	20,575	38,606	11.11
ACI	1.00	1	501	1709	10,975	3.41
ACI	0.10	2	2837	14,446	26,020	5.09
ACI	0.40	2	1537	3824	6836	2.49
ACI	0.60	2	865	4478	—	5.18
ACI	1.00	2	369	845	—	2.29

Process 1 = phosgenation absent TEA; process 2 = phosgenation in presence of TEA.

Figure 1 GPC analysis of 0.06 m/m MAC PC prepared by process 1.

Figure 3 GPC analysis of 1.0 m/m MAC PC prepared by process 2.

weight MAC PCs was obtained by adding MACl to the interfacial mixture containing a catalytic amount of TEA (process variation 2). MACl was added to an interfacial mixture of BA and 0.10 m/m TEA with 50% aqueous sodium hydroxide added to maintain an aqueous phase pH of 9 (Scheme 2). TEA serves both as a phase transfer catalyst for BA and activates the acid chloride towards nucleophilic displacement, as for the case in the reaction of phosgene with BA and the cou-

pling of chloroformates.[16] The advantage of using TEA instead of another phase-transfer catalyst is that a tertiary amine such as this is already required, so no additional chemicals would be needed in their manufacture. GPC of this product gives the expected molecular weight based on the amount of chain terminator used (Table I) and shows the expected polymodality due to the high concentrations of low molecular weight components (Fig. 5). LC shows greater relative concen-

Figure 2 LC analysis of 0.06 m/m MAC PC prepared by process 1.

Figure 4   LC analysis of 1.0 m/m MAC PC prepared by process 1.

Scheme 2   Synthesis of (M)AC PCs by the TEA modified interfacial process.

Figure 5 GPC analysis of 1.0 m/m MAC PC prepared by process 2.

trations of oligomers compared to BA dimethacrylate (Fig. 6). However, the area ratios of these oligomers in both the LC and GPC analyses are skewed by the greater molar absorbance at the UV detector wavelength used (264 nm) of the aryl ester[17] compared to the aryl carbonate[18] chromophore.

Process variation 2 was also used to prepare higher molecular MAC PCs (0.50 m/m and 0.70 m/m). GPC and LC analyses of these products

show the trends in polymodality and oligomer distribution as described above for 1.0 m/m MAC PC (Table 1). Because the molecular weight distributions obtained by this process are as expected for the amount of chain terminator employed, it can be deduced that the degree of hydrolysis of the added MACl is low.

Synthesis of AC PCs

AC PCs prepared by process 1 (Scheme 1) have bimodal GPC peaks and relatively high molecular weights using both low and high amounts of ACl (Table I). The 0.10 m/m AC PC shows two well-resolved peaks in its GPC curve (Fig. 7); the later peak is tentatively identified as BA-diacrylate. LC analysis of this product shows a large early eluting peak having an aryl ester-type UV spectrum and a retention time corresponding to BA-diacrylate, and a narrow polymer peak having a typical aromatic carbonate UV spectrum (Fig. 8). A 1.0 m/m AC PC prepared in the same manner gave a higher than expected molecular weight (Table I) and also displayed a bimodal GPC curve and a predominant BA-diacrylate peak in its LC. Using process variation 2 (Scheme 2), both low and high molecular weight AC PCs were prepared having narrower molecular weight distributions. The 0.10 m/m AC PC shows a much smaller BA-diacrylate peak in its GPC and LC chromato-

Figure 6 LC analysis of 1.0 m/m MAC PC prepared by process 2.

Figure 7 GPC analysis of 0.10 m/m AC PC prepared by process 1.

Figure 9 GPC analysis of 0.10 m/m AC PC prepared by process 2.

graphs (Figs. 9 and 10). The use of increasing amounts of ACl produced PCs having decreasing molecular weights and increasing amounts of BA-diacrylate (Table I). The M_w of 0.60 m/m AC PC is higher than expected due to the presence of a high molecular weight fraction of unknown origin in this sample. As with MAC PCs, the differing UV absorbencies of the aryl ester and aryl carbonate components in AC PCs are not corrected in these GPC and LC analyses. Based on the molecular weight distributions obtained, it is estimated that

little of the added ACl hydrolyzes (and thereby does not chain terminate) in the course of process variation 2.

Crosslinking of (M)AC PCs

The thermal crosslinking behavior of MAC PCs depends on their initial molecular weight. High molecular weight 0.06 m/m MAC PC formed no gel fraction after heating for 30 min each at 150 and 200°C (Table II). These conditions were cho-

Figure 8 LC analysis of 0.10 m/m AC PC prepared by process 1.

Figure 10   LC analysis of 0.10 m/m AC PC prepared by process 2.

sen because of their proven applicability to crosslink maleimide-terminated PCs[17] and to avoid possible methacrylate reaction product degradation[18] at higher temperatures. The use of 2 wt % dicumylperoxide (DCP) with these conditions provided a crosslinked material having 74% gel. An azo initiator (VAZO 88), which has about the same half-life temperature as DCP, gave far less crosslinking.

Low molecular weight MAC PCs thermally crosslink to give nearly complete network formation. 0.50 m/m MAC PC gave 94% gel after crosslinking at 225°C for 1 h with 2% DCP (Table II). Longer curing at higher temperatures gave less gel, presumably due to thermal degradation of the methacrylate oligomer network junctions formed during crosslinking. 0.70 m/m MAC PC gave only 26% gel after 30 min at 150°C and then

Table II   Crosslinking of MAC PCs

m/m	Time (min)	Temp. (°C)	Additives (wt %)	Wt % Gel
0.06	30	150, 200	—	0
0.06	30	150, 200	2% DCP	74
0.06	30	150, 200	2% VAZO 88	15
0.50	60	225	2% DCP	94
0.50	120	250	2% DCP	78
0.70	30	150, 200	—	26
0.70	30	150, 200	2% DCP	80
1.00	30	150, 200	—	97
1.00	30	150, 200	2% DCP	98
1.00	3	150	2% DCP	61
1.00	30	150, 200	1% DCP + 0.5% BHT	93
1.00	30	150, 200	1% DCP + 1% BHT	95
1.00	30	150, 200	1% DCP + 2% BHT	93
1.00	30	150, 200	1% DCP + 4% BHT	90
1.00	30	150, 200	2% DCP + 1% BHT	99
1.00	30	150, 200	2% DCP + 4% BHT	93

Figure 11. GPC analysis of 1.0 m/m AC PC prepared by process 2.

Table III Crosslinking of AC PCs

m/m	Time (min)	Temp. (°C)	Wt % Gel
0.10	30	250	98
0.10	30	300	95
0.40	20	250	92
0.60	30	250	97
1.00	5	250	90
1.00	8	250	95
1.00	13	250	99
1.00	30	250	100

for 30 min at 200°C, but with addition of 2% DCP the gel fraction increased to 80%. MAC PCs (1.0 m/m) crosslink with or without added initiator with heating under the above conditions to form greater than 90% gel. This material reacts rapidly at the lower temperature in the presence of DCP, giving about 60% gel in only 3 min. To possibly delay the onset of gelation in the preparation of coatings with this material (see below), a free radical inhibitor, BHT, was added with the initiator. Various combinations of DCP (1 and 2%) and

BHT (0.5–4%) gave upon curing a high gel fraction product.

Both low and high molecular weight AC PCs thermally crosslink to near complete network formation without added free radical initiators. AC PC (0.10 m/m) crosslinked to 98% gel after 30 min at 250°C (Table III). This thermoset also gave a high gel fraction at 300°C, indicating a substantially increased thermal stability over crosslinked MAC PCs. AC PCs (0.40 and 0.60 mm) crosslinked to high gel content under similar conditions. AC PC (1.0 mm) crosslinks rapidly at 250°C, giving 90% gel in only 5 min and 99% gel within 13 min.

(M)AC PC Coatings on BA PC

(M)AC PC coatings on BA PC were prepared for weathering and abrasion-resistance studies. Bub-

Figure 12. LC analysis of 1.0 m/m AC PC prepared by process 2.

Figure 13   Abrasion resistance of crosslinked 1.0 m/m (M)AC PC-Coated PCs.

ble-free coatings were obtained by depositing a 27% solution of 1.0 MAC PC in dichloromethane on a sheet of 0.002″-thick aluminum in an area to cover the BA PC plaque, and then evaporating the solvent. A coating mold prepared from two aluminum sheets was placed on the the BA PC plaque (in its mold), followed by the MAC PC deposited sheet. This assembly was briefly compression molded at a relatively low temperature to spread the material uniformly over the plaque. Crosslinking was performed in a 200°C oven, and then the assembly was again compression molded at this temperature to remove any warpage. This solvent based procedure proved more effective in producing uniform and bubble-free coatings than did the use of BHT inhibited dry powders of MAC PC.

A similar, yet simpler technique was employed to prepare AC PC-coated BA PC plaques. Solutions of AC PCs were applied to an aluminum sheet and evaporated as described above, but crosslinking was done solely by compression molding at high temperature to give uniformly coated BA PC plaques. Apparently this simpler technique worked well with AC PC and not with MAC PC, due to the better thermal stability of the latter.

Using optical microscopy, the average thickness of the AC PC coating was measured to be 400 microns, while the average thickness of the MAC PC coating was 250 microns. Although these thicknesses are higher than the 50-micron coating mold used, they varied very little across the plaques, indicating good uniformity in the coat-

ings. The coated plaques were all completely transparent, and the coatings added little or no color to similarly treated uncoated BA PC.

Surface Hardness of (M)AC PCs

Surface hardness is a critical material parameter necessary to achieve abrasion resistance for hard-coated polycarbonate.[3] Pencil hardness evaluations were, therefore, used to give preliminary indications regarding the abrasion resistance of crosslinked 1.0 m/m MAC PC films. Crosslinked 1.0 m/m MAC PC films all had significantly harder (3H) surfaces than BA PC (HB), and crosslinking conditions and the use of DCP and BHT did not affect the surface hardness of these samples. The hardness of AC PC coatings increased with increasing crosslink density of the AC PC; 0.10 m/m = B, 0.4 m/m = HB, 0.6 m/m = 2H, and 1.0 m/m = 3H.

Abrasion Resistance of (M)AC PCs

The abrasion resistance of the (M)AC PC materials was evaluated by monitoring the development of haze as the material was subjected to abrasive wear. The % haze increase of crosslinked 1.0 m/m MAC PC and 1.0 m/m AC PC-coated BA PC is much lower than that of uncoated BA PC (Fig. 13). For many practical uses a % haze increase of about 10–15% after 500 abrasive wear cycles is required, and this criteria is met by both coated samples. The effect of the crosslink density on the

DELTA % HAZE

Figure 14 Abrasion resistance of AC PC of different crosslink densities.

abrasion resistance of the AC PC coatings shows that the ultimate % haze increase is largely determined by the initial rate of wear (Fig. 14). The final % haze values follow the trend expected based on the coating pencil hardness results.

The AC PC coating experienced much less haze development than the MAC PC material between 50 and 400 cycles of wear. Using optical microscopy, the (M)AC PC coatings were determined to wear through a "chipping" type of mechanism where the coating is progressively worn away during abrasion. Due to the thickness differences between these coatings, the MAC PC coating was probably removed earlier in the abrasive wear test than the AC PC coating, accounting for the MAC PC sample experiencing significantly higher haze increases than the AC PC sample at early wear cycles. Later in the test, the AC PC coating was also worn away, resulting in an equivalent haze increase by both samples by the end of the test.

Weatherability of (M)AC PC-Coated BA PCs

Abrasion-resistant coatings are typically used in applications where ultraviolet light (UV) exposure will occur, and therefore, they must be highly weatherable to retain optical properties. BA PC plaques coated with crosslinked 1.0 m/m MAC PC, 0.5 MAC PC, and 1.0 AC PC, as well as an uncoated plaque, were exposed to accelerated weathering in a xenon arc weatherometer. Both the MAC PC and AC PC coated samples increased in YI to an equivalent degree as the uncoated BA

PC sample (Table IV). This indicates that the (M)AC PC coatings could retain optical properties long term through the use of appropriate UV absorbers. However, a significantly higher % haze increase in the MAC PC-coated plaques was found compared to the AC PC and uncoated plaques.

Optical microscopy was used to assess the appearance of the samples after weathering exposure to understand the significant haze increase differences between the MAC PC and AC PC coatings. The MAC PC coated samples had highly concentrated microcracks, while the AC PC coating had very fine microcracks that were not highly concentrated. The highly concentrated microcracks in the MAC PC diffract more light and cause the hazy appearance. The cause of these crack formation differences is unknown, but may be related to the relative thinness of the MAC PC layer.

Although both the AC PC-coated BA PC and the uncoated BA PC had experienced greater

Table IV   Weathering Behavior of (M)AC PC Coated PCs

Coating	Δ YI[a]	Δ % Haze[b]	Δ % T[b]
none	17	25	−2.0
1.0 m/m MAC PC	15	62	
0.5 m/m MAC PC	12	60	
1.0 m/m AC PC	20	20	−1.5

[a] After 3000 h.
[b] After 2500 h.

than 20% increases in haze, the transmission of the samples was affected very little (Table IV). The coated sample had a somewhat lower overall transmission than the uncoated BA PC due to diffraction of the light at the coating/substrate interface. Overall, the weathering behavior of the (M)AC PC coatings indicate that these materials do not weather significantly differently than BA PC.[21]

CONCLUSIONS

(M)AC PCs were prepared under interfacial conditions by reaction of (meth)acryloyl chloride with BA followed by phosgenation. Addition of (M)ACl to an interfacial mixture of BA containing a catalytic amount of TEA gave linear polymers having a narrower molecular weight distribution. The use of TEA greatly reduced the formation of BA di(meth)acrylates, the key to forming polymers having the expected molecular weights. A series of polymers having M_ws from about 19,000 to about 900 daltons were prepared for crosslinking and property evaluations.

Thermal crosslinking of MAC PCs was achieved generally only in the presence of DCP free radical initiator. Between 75 and 98% gel was obtained by using 2 wt % initiator and heating for 30 min each at 150 and 200°C. On the other hand, the lowest molecular weight MAC PC (1.0 m/m) crosslinked with heat alone under the above conditions. All of the AC PCs crosslinked without added initiator to form 92–100% gel by heating for 30 min at 250°C. Only a slight trend of increasing % gel with increasing (M)AC content was observed.

Coatings of high crosslink density (M)AC PCs on linear BA PC plaques were prepared by a combination of solvent casting, compression molding, and (optionally) oven curing. Moderate to high crosslink density (M)AC PC coatings showed relatively high pencil hardness values and good abrasion resistance. The relatively low degree of haze formation in these coatings was produced by a chipping mechanism, which is typical for hard coatings such as these. In weathering studies, both MAC- and AC PC-coated plaques showed low YI increases, but the MAC PC coating developed higher haze due to microc-

racking. The weathering of AC PC coatings generally followed the performance of unstabilized BA PC, so that conventional UV absorbers are expected to provide adequate protection for these coatings in weatherable applications.

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