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Radiation crosslinking of bisphenol-a polycarbonate in the presence of bisphenol-a dimethacrylate and triallyl cyanurate

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Summary

Radiation crosslinking of bisphenol-A polycarbonate (PC) was carried out by the γ-irradiation of the polymeric films containing 5 and 2 wt % of bisphenol-A dimethacrylate (BPDMA) or triallyl cyanurate, respectively, as well as by the BPDMA grafting from acetone solution onto PC preirradiated in air. The modified samples were analyzed for the sol/gel content, and the dependences of gel fraction yield of crosslinked polymer on monomers concentration and absorbed dose were found. The radiation-chemical yields of crosslinking and degradation as well as gelation doses were determined for the modified PC. Molecular weights of the starting and irradiated pure PC were detemined by the GPC method, and radiation-chemical yield of PC degradation was calculated. It has been found essential difference in efficiency of PC crosslinking depending on monomers and doses used as well as on methods of modification. Effects of crosslinking agents distribution in the PC matrix and simultaneous processes of crosslinking and degradation in the polymer-monomer compositions on efficiency of PC crosslinking have been discussed.

Introduction

Effects of ionizing radiation on properties of bisphenol-A polycarbonate (PC) have been investigated by many workers (1-8). It has been shown that PC irradiation results in its scission.

Radiation crosslinking of polymers, including those degradable under the action of ionising radiation, is often carried out in the presence of crosslinking monomers of various functionality. In some cases, such crosslinking agents are highly efficient even at low concentration (9-20). Triallyl cyanurate (TAC) was successfully used for radiation crosslinking of different polymers (10, 12, 13, 15, 18).

There seem to be no data on radiation crosslinking of PC but earlier we have shown (21) that radiation grafting of acrylic acid (AAc) onto PC was accompanied with partial crosslinking this polymer. Relatively low yield of gel fraction (30-35%) of the crosslinked polymer at the grafted polyAAc concentration of 12-15% has been explained by insufficient efficiency of AAc as a crosslinking agent.

This work presents the results of a study on radiation crosslinking of PC films in the presence of small amounts of bisphenol-A dimethacrylate (BPDMA) or triallyl cyanurate (TAC). Crosslinking was achieved either by irradiation of the PC films that already contained BPDMA or TAC, or by grafting of BPDMA from its acetone solution onto preirradiated films made of pure PC.

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Experimental

PC pellets (Lexan, LBW248) were supplied by General Electric Co., BPDMA and TAC were obtained from Aldrich Chemical Co. PC films (100-120 μm thick) were cast from a 5% solution of the polymer in dichloromethane into a Petri dish. BPDMA- or TAC-containing films were obtained from the same polymer solution in the presence of these monomers of different concentrations. All films were exposed to air at room temperature for 1 day, and pure PC films were additionally kept under vacuum for 2 to 3 h to remove the residual solvent (gravimetrical control).

The PC pellets and BPDMA- or TAC-containing films were placed in glass ampoules, deaerated and sealed under vacuum, and irradiated with a ^{60}Co γ-source (Gammabeam 651 PT, Nordion International Inc.) at a dose rate of 7 kGy/h and doses from 50 to 400 kGy. The irradiated BPDMA or TAC-containing samples were outgassed for 2 to 3 h in vacuum at room temperature to a constant weight.

Molecular weights of the starting and irradiated PC pellets were detemined by the GPC method. The chromatograph was equipped with a pump (Varian 9002), column TSK-gel type 64000H8 connected with detector of refractometer (Varian RI-4) and integrator (Varian 4400) supplied with GPC-Plus software. Chloroform (Chrom AR, grade HPLC) was used as an eluent. The system was calibrated with polystyrene TSK standard (TOSOH, Japan).

For the swelling of PC in BPDMA-acetone solution to be characterized, PC films were immersed in 20 wt % solution of BPDMA in this solvent at room temperature until equilibrium swelling was reached. Then samples were taken out and the excess solution deposited on the film surface was removed quickly with blotting paper, and samples were weighed. The swelling degree was calculated by the equation:

$$\text{swelling (\%)} = (W - W_o)100/W_o$$

where W and W_o are the weights of swollen and dry samples, respectively.

For grafting by the preirradiation method, the PC films were irradiated in air at a dose rate of 7 kGy/h and doses from 50 to 120 kGy. The irradiated samples were placed in glass ampoules which contained 20 wt % solution of BPDMA in acetone. The ampoules were kept under argon flow for 30 min, then sealed and placed in water bath at 70°C for 1 h. The modified films were washed with acetone for 24 h to extract unreacted BPDMA, dried under vacuum for 1 day to a constant weight. The grafting yield was determined gravimetrically as weight percent of the grafted polyBPDMA in the modified PC.

For gel fraction analysis, all the modified films were immersed in dichloromethane for 24 h. The insoluble residue was outgassed in vacuum for 2 to 3 h to complete removal of the solvent. The yield of gel fraction was determined in reference to the weight of modified sample.

Results and discussion

PC films in the presence of BPDMA were transparent up to 20-25 wt % of this addition but they became opaque at the TAC concentrations 10 wt % and more. Apparently, this transparency deterioration at a relative low TAC concentration was caused by heterogeneity of the obtained polymer-monomer compositions resulting from

unsatisfactory compatibility of the components and non-uniform distribution of TAC in the PC film. Transparency of films at the TAC concentrations less than 10 wt % may be explained by a small particles size in the dispersed phase. Irradiation of pure PC as well as BPDMA- and TAC-containing samples (2-10% of these additions) up to 400 kGy did not lead to increased fragility but samples became yellowish.

Fig.1 shows optimal BPDMA and TAC concentrations (5 and 2%, respectively) for the maximal efficiency of PC crosslinking at the dose used. On further increase in monomers concentrations the gel fractions yields increased practically proportionally to amounts of monomers introduced, i.e., polyBPDMA or polyTAC, formed due to irradiation, contributed to the gels yields.

Different efficiency of the PC crosslinking in the presence of BPDMA or TAC may be explained by different distribution of the crosslinking agents in PC resulting from their compatibility. On the other hand, a relatively low yields of gel fractions in both cases may be caused by the method used to obtain polymer-monomer compositions. Probably, formation of these compositions from their solutions in a appropriate solvent (dichloromethane is the preferred solvent for obtaining of PC films) leads to insufficient uniform distribution of monomers in polymer matrix in comparison with well-known method of polymers and monomers mixing in a Brabender plasticorder at an elevated temperature (12,14,15,18). But our preliminary experiments to mix PC powder with BPDMA or TAC at temperatures within 200-250°C (PC melts at these temperatures) resulted in absence of PC crosslinking caused, apparently, by thermal instability of methacryl or allyl groups of the crosslinking agents used at these high temperatures. In our case, essential part of TAC may form a separate phase inside the starting polymer,

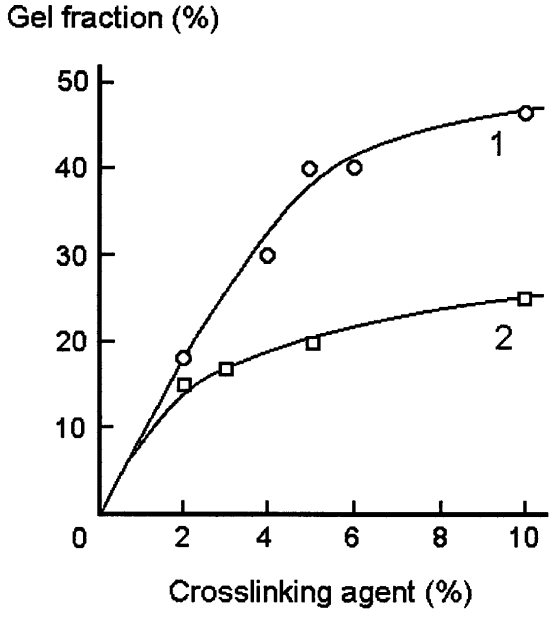

Fig.1. The yield of gel fraction as a function of BPDMA (1) and TAC (2) concentration in modified PC. Dose =100 kGy.

and irradiation of this composition will result in considerable amount of polyTAC homopolymer that will not serve as a crosslinking agent for PC. Apparently, this negative process occured to a essentially less extent for the BPDMA-containing films. The polyTAC and polyBPDMA homopolymers are insoluble in organic solvents due to their crosslinked state, and can not be removed from the modified PC. It is reasonable to assume that PC crosslinking is also accompanied by graft polymerization of BPDMA and TAC. In an ideal case, every BPDMA or TAC molecule should react with the active centers of the irradiated PC to form short crosslinks. In reality, some amount of these monomers are involved in formation of long grafted chains, which also crosslink the substrate polymer through termination by interaction with each other or with radicals of the irradiated PC. The proportions at which these crosslinking agents are consumed in the competing reactions of crosslinking and grafting are difficult to estimate. The polyBPDMA and polyTAC homopolymers and grafted chains contribute to the experimentally determined yields of insoluble fractions but this contribution is small because the total amounts of the insoluble fractions is much greater than that of crosslinking agents introduced at their low optimal concentrations into the polymer.

The dose dependence of PC crosslinking efficiency in presence of the crosslinking agents used is shown in Fig.2. The gelation doses (D_g) were determinated by graphical extrapolation to zero gel fraction for the curves representing the dose dependence for the yield of gel fraction, and D_g values are close to 50 kGy. It is seen that the optimal dose for gel accumulation is 100 kGy for BPDMA- and TAC-containing samples. On further irradiation the yield of the gel fractions tends to decrease, which can be explained by scission of some PC fragments from the crosslinked polymer by γ-irradiation and their transition to the sol fraction. Fig.2 shows that this decrease is more essential for the BPDMA-containing films. Probably, this effect is caused by the additional partial scission of the polyBPDMA crosslinks at doses more than 100 kGy when process of crosslinking was completed due to BPDMA exhaustion. To verify this assumption,

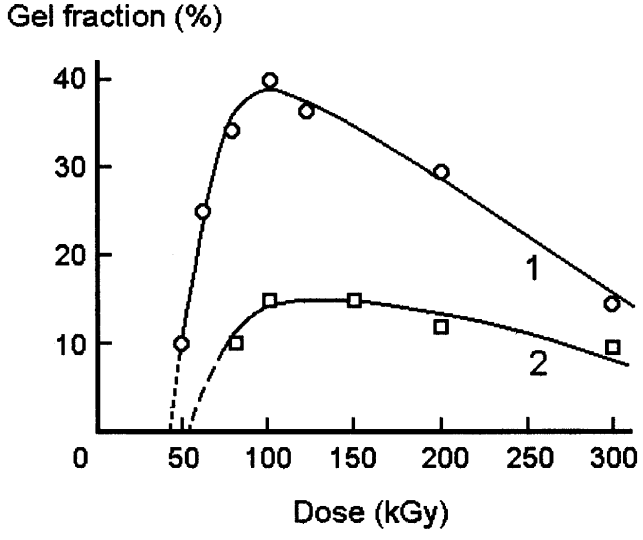

Fig.2. The yield of gel fraction in modified PC as a function of dose.
BPDMA (1) and TAC (2) concentrations are 5 and 2%, respectively.

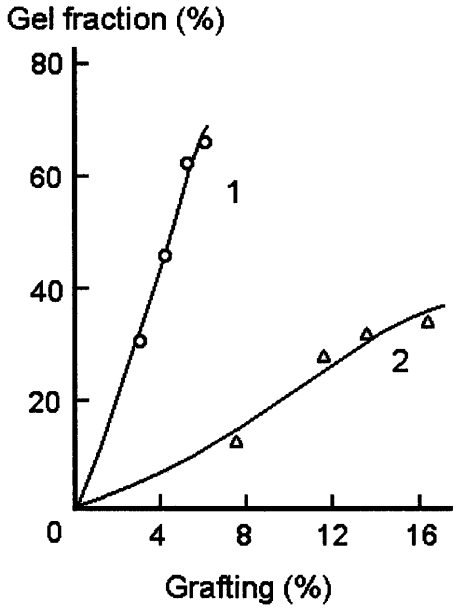

Fig.3. The yield of gel fraction as a function of grafted polyBPDMA (1) and polyAAc (2) contents in modified PC.

radiation grafting of BPDMA was carried out onto PC by the preirradiation method. Grafting of monomers onto polymers preliminary irradiated in the presence of air is widely used for polymers modification (22). In this case, a modifying monomer and grafted polymer formed from it are not subjected to irradiation. PC swelled well in BPDMA-acetone solution and the equilibrium swelling was equal to 40% that ensured effective penetration of monomer into the PC film (21). 70°C is an appropriate temperature for peroxides and hydroperoxides thermal decomposition in irradiated PC to form active centers for grafting initiation (21). PC films with grafting values from 3 to 6% were obtained at the preirradiation doses from 50 to 120 kGy. BPDMA homopolymerization was practically absent (visual control of viscosity changes in monomer solution) under these conditions (doses of preirradiation, temperature and time of grafting). Fig.3 shows essential increase in gel formation for grafted PC films as compared with samples that already contained BPDMA in PC before irradiation. Curve 2 was reproduced from our previous work (21) with permission from Elsevier Science to illustrate essential difference in efficiency of the PC crosslinking depending on monomer used for grafting onto this preirradiated polymer. Thus, it is possible to conclude that irradiation of PC-BPDMA composition resulted in simultaneous crosslinking and degradation processes up to optimal dose of gel accumulation with following essential scission both PC macromolecules and polyBPDMA crosslinks on their further irradiation. The radiation-chemical yields of polymer crosslinking (G_c) and degradation (G_d) were determinated from the gel fraction build-up curves (Fig.2) using the Charlesby-Pinner equation (20,23):

$$s + s^{0.5} = \frac{50 N_A}{\overline{M_n} G_c D} + \frac{G_d}{G_c}$$

where s is the sol fraction, N_A is the Avogadro number, $\overline{M_n}$ is the number-average molecular weight of PC prior to irradiation, and D is the absorbed dose. The G_d/G_c ratio was determined by graphical extrapolation of the linear $s+s^{0.5}$ vs.1/D dependence to $D \to \infty$. The G_c and G_d values were determined with accuracy to ± 5%.
It should be noted that concentration of polyBPDMA in PC depended on preirradiation dose in samples made via grafting. In this case, determination of the G_d/G_c ratio with following G_c and G_d calculations were made for samples with the polyBPDMA content from 4 to 6%, i.e., at concentrations of the crosslinking agent close to that one in films formed from PC solution in dichloromethane contained 5% of BPDMA. These parameters could not be determined reliably for TAC-containing samples because of very low gel fraction yields in this case, only G_d/G_c ratio was roughly estimated as 1.3-1.5.

For the initial PC, G_d was determined from the $\overline{M_n}$ vs. D dependence (Fig.4) using the Charlesby equation (24):

$$G_d = \frac{9.65 \cdot 10^3}{D}\left(\frac{1}{\overline{M_n^D}} - \frac{1}{\overline{M_n}}\right)$$

where $\overline{M_n^D}$ is the number-average molecular weight of the irradiated PC.
It is seen from Table 1 that both G_c values are practically the same, but G_d and G_d/G_c ones sharply changed depending on method of PC modification in the presence of BPDMA. This difference indicates essential effect of degradation by direct irradiation of the PC-BPDMA composition that decreased efficiency of the PC crosslinking.

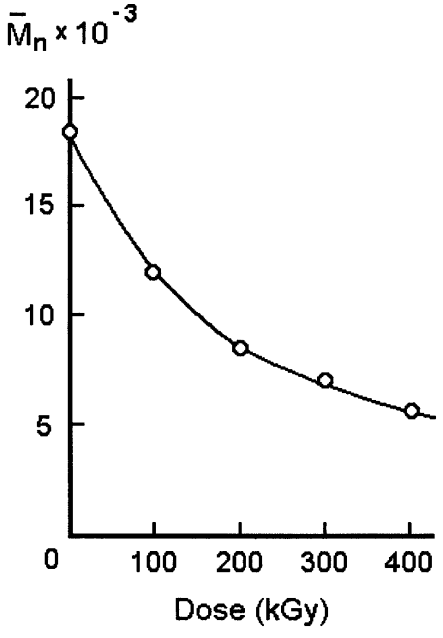

Fig.4. The dose dependence of the PC molecular weight.

Table 1. Radiation-chemical parameters of crosslinking and degradation for starting and modified PC.

Parameter	Starting PC	PC-BPDMA (5%) irradiated	PC grafted with polyBPDMA (4-6%)
G_c , crosslinks/100eV	0	4.0	3.8
G_d , scissions/100 eV	2.8	2.4	1.5
G_d/G_c	-	0.6	0.4

Conclusion

Efficiency of PC radiation crosslinking in the presence of BPDMA or TAC depended on monomer used, its concentration, dose of irradiation as well as on method of modification. Gel fraction of the crosslinked PC reached 40% in BPDMA-containing samples at 5% of this monomer and dose of 100 kGy. Approx. 1.6-fold increase in a gel fraction yield has been found at BPDMA grafting onto preirradiated PC that can be explained by absence of scissions in crosslinks between PC macromolecules. Radiation crosslinking of the TAC-containing PC was essentially less caused, probably, by non-uniform distribution of TAC in the PC matrix resulting from their unsatisfactoty compatibility.

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