

# Photoinduced Crosslinking of Polyolefine Blends. I. Crosslinking of LDPE, PP, and LDPE/PP Blends

P. ZAMOTAEV,<sup>1</sup> I. CHODAK,<sup>2,\*</sup> O. MITYUKHIN,<sup>1</sup> and I. CHORVATH<sup>2</sup>

<sup>1</sup>Institute of Bioorganic and Oil Chemistry, Ukraine Academy of Science, Kharkovskoe shosse, 50 253 160 Kiev, The Ukraine; <sup>2</sup>Polymer Institute, Slovak Academy of Science, Dubravska cesta, 842 36 Bratislava, Slovak Republic

## SYNOPSIS

Photocrosslinking of low-density polyethylene (LDPE), polypropylene (PP) and their blends was investigated using xanthone and triallyl cyanurate as a photoinitiator and a coagent, respectively. The influence of the change of UV-irradiation conditions on the yield of photoinitiated processes was found to be very similar at any composition, while the crosslinking efficiency decreases with increase of PP content in the blend. The mechanism of the TAC action in photocrosslinking process was proposed and the effect of TAC reactions is discussed with regards to the effectivity of crosslinking of LDPE, PP, or the blends. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

An important approach to the development of the specialty polymer materials is based nowadays on the combination of different polymers into a new products having some of the desired properties of each component. One of the main obstacles to achieve this target is the inherent incompatibility of most polymer combinations, resulting in the deterioration of mechanical properties of the blends. It usually occurs because, due to the poor interfacial adhesion, the imposed stress cannot be sufficiently transferred between the different phases in the blends with heterogeneous structure.

Considering the number of commodity polymers, the blending of isotactic polypropylene (PP) with polyethylene (PE) in order to improve the processability, impact strength, and some other properties is of great interest.<sup>1-7</sup> The combination of these two polymers is of interest also when recycling is considered.<sup>6</sup> The improvement of the blend properties is possible to some extent through the control of the fabrication process, but is mostly achieved by addition of compatibilizers, resulting

in an increase of the interaction between PE and PP phases.<sup>6-9</sup>

Crosslinking is another possibility for influencing the interaction between the phases.<sup>10</sup> Attempts have been made to increase PE/PP blends' compatibility by radiation<sup>11-13</sup> or peroxide-induced crosslinking.<sup>5,7,14,15</sup> However, the crosslinking efficiency in PE differs very much from that in the PP phase since PP macromolecules undergo scission rather than crosslinking in the course of radical reactions.<sup>16-18</sup> PP degradation can be suppressed by addition of coagents, such as phenols, quinones,<sup>15</sup> or multifunctional allylic monomers if the crosslinking is initiated by peroxides.<sup>14</sup> However, even in this case, a high processing temperature of PP-rich blends makes the melt-compounding of conventional initiators and coagents difficult due to the premature peroxide decomposition.

It was shown that the two-phase structure of PE/PP blends is preserved either after melt or solid-state crosslinking,<sup>6-15</sup> but in the former case, the morphology is changed,<sup>6,12,14,15</sup> affecting also the mechanical properties.<sup>4,5</sup> A certain degree of co-crosslinking between PE and PP chains on the interface was deduced from the mechanical,<sup>5,7</sup> DSC, density,<sup>12,13,15</sup> and extraction data.<sup>14</sup> On the other hand, extensive microscopic, thermal, mechanical, and chromatographic studies of PE/PP blends modified by a small amount of dicumyl peroxide during the

\* To whom correspondence should be addressed.

extrusion process do not reveal any strong evidence supporting PE-PP copolymers formation under given processing conditions.<sup>6</sup>

This work is an attempt to investigate the possibility of PE/PP blend compatibilization by photocrosslinking.<sup>19-21</sup> Since photoinitiators and coagents can be easily melt-compounded at high temperature and UV light results in less drastic degradation of PP,<sup>22,23</sup> compared to ionizing radiation,<sup>17</sup> photocrosslinking could be appropriate for PE/PP blend modification. An additional potentially beneficial factor consists of the possible preferential sorption of the low molecular weight additives in the interfacial region.<sup>24</sup> It might result in increased concentration of initiators and coagents in the interfacial region, leading to enhanced yields of the photoinitiated processes there. On the other hand, photocrosslinking is applicable only for modification of foils or thin slabs (up to 0.5–1 mm, depending on content and quality of UV-absorbing species) or surface layers of bulky products.

## EXPERIMENTAL

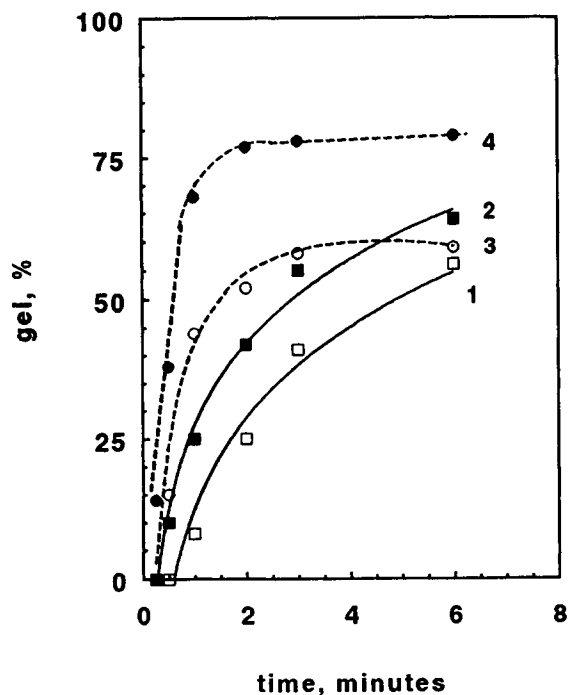
Low-density polyethylene (LDPE, Bralen RA 2-19, Slovnaft, Slovakia, MFI = 2.0 g/10 min) and isotactic polypropylene (Tatren MD 100, Slovnaft, Slovakia, MFI = 3.7 g/10 min) were used in this work as received. Both polymers contain a small amount of BHT as a high-temperature processing antioxidant. The photoinitiator xanthone (XN, Erivan, chemreactive) and the coagent triallyl cyanurate (TAC, Fluka AG) were used as received. The blends were melt-compounded in an internal Brabender PLE 331 mixer (volume of the mixing chamber 60 mL) at 190°C and 75 rpm for 8 min. The additives (XN or XN and TAC) were premixed with polymers before melt-compounding. The concentration of the additives was 0.3% of XN and 2.0% of TAC in all samples. After mixing, 0.4 mm-thick films were compression-molded at 180°C for 1 min. The UV irradiation was carried out by full lights of a medium-pressure mercury lamp DRT-1000 (1000 W) in air. The time between the foil preparation and irradiation was diminished as much as possible in order to decrease XN and TAC diffusion to the surface, especially noticeable in PE-rich blends. During UV irradiation, the samples were placed on a copper heating element and fixed by a quartz glass. The temperature was recorded by a thermocouple and controlled to  $\pm 3^\circ\text{C}$ . The gel content was determined as the weight of the insoluble part in the sample after 14 h extraction in boiling xylene. Some

samples were first extracted for 14 h in boiling cyclohexane, then dried, weighted, and extracted in xylene.

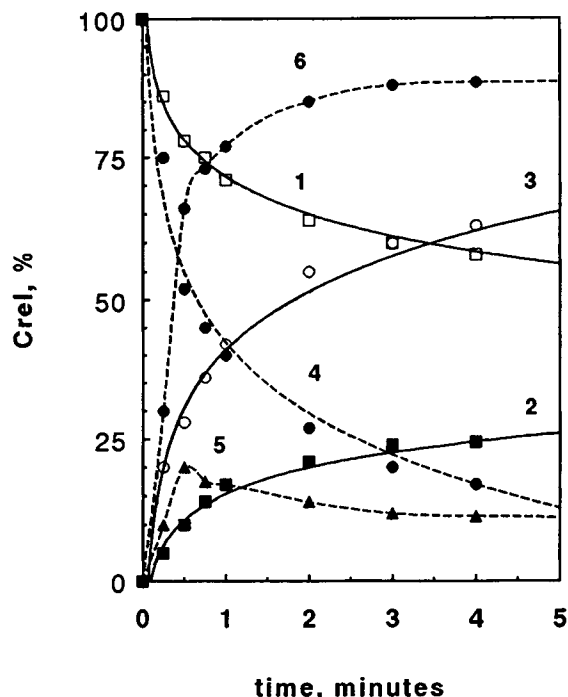
Infrared (IR) analysis of the foils was performed using a Specord 71 IR spectrometer while electron absorption and emission spectra were recorded by Specord M40 and equipment constructed from commercial devices based on a monochromator MDR-12.<sup>19</sup> The consumption of TAC allyl groups were determined by the decrease of vinyl absorption peak intensity at 1000 and 955  $\text{cm}^{-1}$  using the peak of triazine ring (820  $\text{cm}^{-1}$ ) as an internal standard.<sup>20-25</sup> The degree of grafting of TAC molecules and percent of unreacted allyl double bonds in grafted TAC molecules were determined by the residual IR absorption in the corresponding bands after extraction of films for 48 h in octane at 60°C and in acetone for the same time at the same temperature.

## RESULTS AND DISCUSSION

Figure 1 represents the gel content vs. UV-irradiation time for LDPE containing only XN or XN and TAC and crosslinked in the solid state and in the



**Figure 1** Gel content in LDPE vs. irradiation time; photocrosslinking was initiated by XN at (1) 30 or (3) 170°C and by XN in the presence of TAC at (2) 30 and (4) 170°C.



**Figure 2** The dependence of the relative concentration of (1, 4) intact TAC allyl double bonds, (2, 5) unreacted allyl double bonds and (3, 6) grafted triazine groups in extracted photocrosslinked LDPE films on irradiation time. The temperature for UV-light exposition was 30 (full line) or 170°C (dotted line).

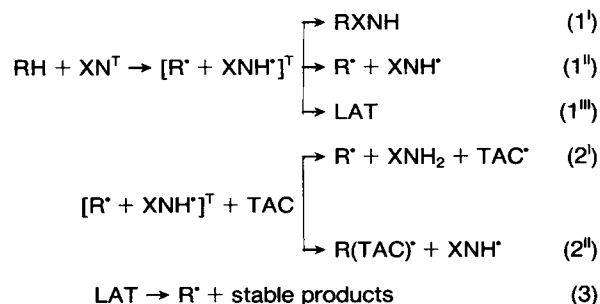
melt. The grafting of TAC molecules and conversion of TAC double bonds are exhibited in Figure 2. It is seen that TAC propensity to increase photocrosslinking efficiency is especially pronounced at high temperatures. Simultaneously, the highest yields of TAC grafting and allyl double-bond conversion are observed. The curves in Figures 1 and 2 are rather steep at the beginning of UV exposition, when photoreduction of the substantial portion of XN molecules occurred, providing the highest output of macroradical initiation reactions.<sup>19,21</sup> Then, with decay of the initiation system, the yield of the photoinitiated process decreases; the gel content, TAC grafting yield, and allyl double-bond consumption degree reached a plateau approximately after 3 min of UV exposition at 170°C and 6–7 min at 30°C.

Both the maximal level of TAC grafting and the allyl bonds consumption substantially exceed the molar concentration of XN, e.g., the maximal TAC grafting degrees are approximately 0.15 (30°C) and 0.21 mol/kg (170°C), whereas the original concentration of XN in LDPE was only 0.015 mol/kg. It is reasonable to assume that the macroradicals generated due to XN photoreduction are partially par-

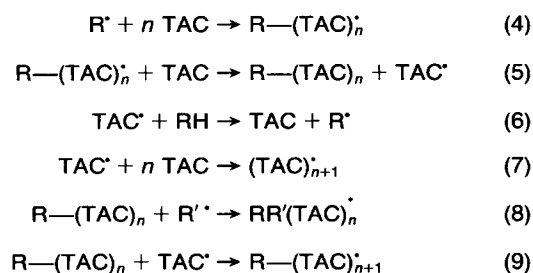
ticipating in other reactions (interchain crosslinking, scission, reactions with oxygen, etc.). Thus, we have to admit that TAC double bonds in the LDPE matrix participate in chain reactions.

The grafting of unsaturated coagents on polymer chains during crosslinking leading to a formation of intermolecular bridges is generally accepted for photo-,<sup>19,20</sup> peroxy-,<sup>14,15</sup> or radiation-initiated processes.<sup>26,27</sup> As a result, the addition of a coagent would prevent the scission and promote the crosslinking in PP<sup>16,17</sup> and to a small extent in branched PE chains where the macroradicals show the tendency to destruction.<sup>27</sup> For example, it was shown recently that crosslinking yield decreased in branched PE because of chain scission after polymer transition from the solid to the molten state.<sup>28</sup> Thus, the largest positive effect of TAC on the crosslinking in the melt can be ascribed partially to the stabilization of macroradicals on tertiary carbon through grafting (Scheme 1, reaction 4). Nevertheless, to ex-

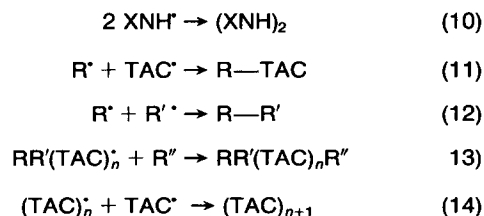
#### I. Initiation:



#### II. Propagation:



#### III. Termination:



**Scheme 1**

plore other possible ways of TAC influence on the photocrosslinking process, it appeared reasonable to discuss all stages: initiation, chain propagation, and termination.

It was shown that UV light passing through PE film generates the  $^3n\pi^*$  excited state of XN ( $XN^T$ ).<sup>19-21</sup>  $XN^T$  decays via hydrogen abstraction from the macromolecule, leading to a radical pair ( $[R^* + XNH^*]$ ) that could recombine in the cage producing grafted xanthidole ( $RXNH$ , reaction 1<sup>I</sup>) or light-absorption transient (LAT, reaction 1<sup>III</sup>).<sup>19</sup> Similar transients are formed in PE as a result of photoreduction of benzophenone, anthrone, or their derivatives.<sup>21</sup> Their phototransformations are accompanied by additional radical initiation (reaction 3). However, the initiation efficiency of this pathway is determined mainly by the radical escape from the cage (reaction 1<sup>II</sup>). The absorption and emission spectra indicate that the addition of TAC leads to a decrease of the yield of dixanthilene ( $XNH$ )<sub>2</sub>. Moreover, a new species, namely, xanthidole ( $XNH_2$ ), has been identified among the reaction products of XN photoreduction in PE.<sup>19</sup> These facts can be considered as indirect evidence of a contribution of TAC molecules to a disintegration of the radical pair  $[R^* + XNH^*]^T$ . This may occur via a decay of  $XNH^*$  radicals by allyl hydrogen abstraction from TAC producing  $XNH_2$  (reaction 2<sup>II</sup>). TAC addition to  $R^*$  saving  $XNH^*$  radicals which recombine to ( $XNH$ )<sub>2</sub> (reaction 10) is also possible.

Concerning the propagation reactions, in addition to reaction 4 mentioned above, the following processes may be considered:

- The abstraction of TAC allylic hydrogen is also possible via chain-transfer process 5.
- Photoinduced transformation of allyl to alkyl radicals in PE was found to be rather effective.<sup>29</sup> Since the formation of TAC<sup>\*</sup> allyl radicals in chain-transfer reactions 2<sup>I</sup> and 5 appears to be highly probable,<sup>20</sup> reaction 6 can compete with homopolymerization or oligomerization processes 4 and 7, suppressing the termination reaction 11.
- Homopolymerization reaction 7 can be anticipated, especially at high temperature,<sup>25</sup> while at ambient temperature, TAC oligomer formation by termination reaction 14 seems to be more probable.
- Reaction 8 is particularly significant because crosslinks are formed and, at the same time, macroradicals are regenerated, while in reaction

8, only transformation of radicals to macroradicals occurs.

Considering the termination processes, it has to be pointed out that formation of the multifunctional junctions may be expected by anchoring more than one macroradical via allyl bonds left intact in TAC-grafted molecules (reaction 13). An idea of the formation of multifunctional junctions during radiation<sup>27,30</sup> or photoinitiated,<sup>31</sup> crosslinking of PE in the presence of TAC is supported by tensile, shrinking, and DSC data. When compared with PE samples crosslinked in the absence of a coagent under the same conditions, the presence of TAC brings about a higher elastic effect and less pronounced depression of the PE crystallization process in crosslinked PE.

In the scheme, no interference of BHT with the processes discussed above was taken into account. This is a rather important topic, since, on the one hand, the presence of thermal antioxidant is unavoidable for obtaining good properties of crosslinked material, especially when containing a higher portion of the PP component. Processing in the absence of BHT resulted in a more or less brittle material, indicating a significant portion of thermal degradation during processing.<sup>32</sup> On the other hand, BHT unreacted during processing should interfere with the crosslinking reaction similar to other phenolic antioxidants.<sup>33</sup> Quantification of the BHT effect on crosslinking is difficult mainly because the antioxidant partially decays due to chemical reactions and partially evaporizes from the reaction mixture during processing; due to rather low BHT concentration, the effect on the crosslinking process should not exceed 10%.<sup>33</sup>

Another item worthy of discussion is a possible thermal reaction of additives during melt processing of the blend. This may be neglected in the case of thermally rather stable xanthone, but some thermal initiation of the TAC double-bond reaction could occur. However, the coagent is commonly used as a radiation yield activator in PE and no problems related to processing were reported. This is supported also by an absence of TAC grafting in the processed samples before UV irradiation, as shown in Figure 2 (curves 3 and 6). Therefore, only a negligible part, if any, of TAC double bonds react during processing of the blends.

The formation of network structures considering the branching efficiency ( $n$ ),<sup>27</sup> the number of consumed allyl groups per one grafted TAC molecule, defined as

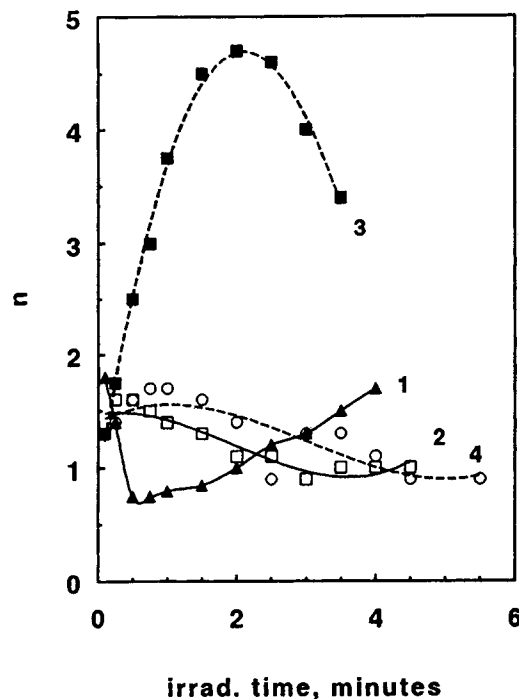
$$n = \frac{\Delta[\text{C}=\text{C}]_c - \Delta[\text{C}=\text{C}]_g}{\Delta[\text{TAC}]_g} \quad (1)$$

where  $\Delta[\text{C}=\text{C}]_c$ ,  $\Delta[\text{C}=\text{C}]_g$ , and  $\Delta[\text{TAC}]_g$ , are the changes of concentration of consumed TAC allyl bonds, the TAC allyl bonds remaining intact in grafted molecules, and the degree of TAC grafting within a certain short period of UV-irradiation time. These values were calculated from the slopes of tangents of the corresponding curves on the concentration vs. time plot (Fig. 2).

A substantial difference in the dependences of  $n$  vs. UV-irradiation time regarding the photocrosslinking of LDPE at 30 and 170°C is obvious (Fig. 3). The  $n$  value is permanently larger than 1 and exceeds three in the interval from 1 to 3 min of UV irradiation when the maximum gel content is reached if the process proceeds in the molten state (Fig. 1). This would also indicate that reactions 8 and 13, leading to the formation of multifunctional intermolecular junctions, are rather important in the melt. Such a conclusion is supported by a reverse course of the dependence of the concentration of unreacted allyl double bonds in grafted TAC molecules becoming apparent after 30 s irradiation, i.e., long before the TAC grafting degree approaches the limiting value (Fig. 2). TAC homopolymerization might be also considered as a reason for high  $n$  levels. Yet, since approximately 90% of TAC molecules appeared to be fixed in PE by grafting, we ought to assume that the TAC oligomers, if formed, have to be grafted successively. This should lead to a drop of  $n$  below 1. This was not observed in the molten LDPE, but occurs at low-temperature photocrosslinking: The value of  $n$  being around 2 at the beginning of irradiation is decreased below 1 (Fig. 3), and at the same time, extensive TAC grafting is observed (Fig. 2). The drop of  $n$  could be attributed to the grafting of TAC oligomers formed at the beginning of UV-light exposition. A further increase of the  $n$  value can be ascribed to the anchoring of some grafted chains to macromolecules. However, the effectivity of this process is much lower at ambient temperature than in molten PE. This is also confirmed by the permanent increase of the amount of unreacted allyl bonds in grafted chains with the degree of TAC grafting at 30°C (Fig. 2).

The crucial influence of temperature on photoinduced processes in LDPE can be attributed to the following phenomena<sup>19-21</sup>:

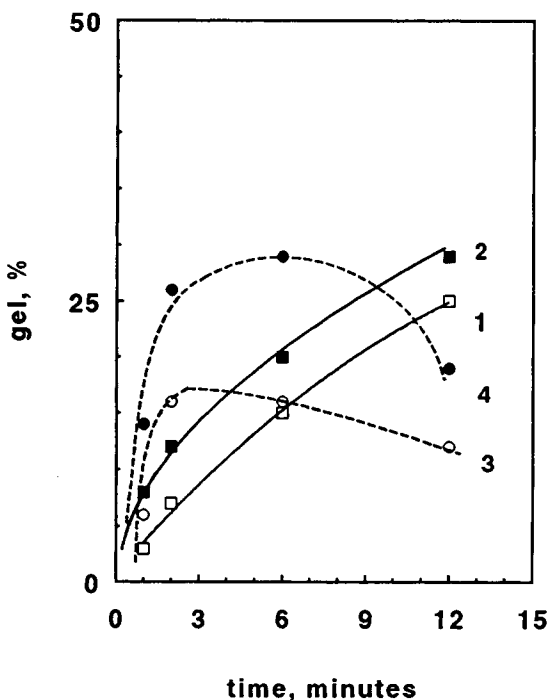
- An increase of macroradical mobility and a decrease of the cage effect with the temperature increase.



**Figure 3** Parameter  $n$  (see text) vs. irradiation time in (1, 3) LDPE and (2, 4) PP. The temperature for UV-light exposition was (full line) 30 or (dotted line) 170°C.

- A decrease of the screening effect imposed by the light-absorbing transients due to their fast decomposition at high temperature.<sup>21</sup>
- The growth of the photoinitiator and coagent miscibility with temperature, resulting in a more homogeneous distribution.

The efficiency of photocrosslinking of PP initiated by XN is lower than that of PE (Fig. 4). Increasing the temperature leads to enhancing the PP crosslinking at the beginning of UV irradiation, but further exposition results in the decrease of the gel content, apparently due to extensive photodegradation.<sup>23</sup> At the same time, no significant peculiarities were observed regarding the xanthone photochemistry in PP. The electron absorption and emission spectra are similar to those observed in LDPE, except for a small ( $100\text{ cm}^{-1}$ ) hypsochromic shift of the main absorption peaks. The rate of XN photo-reduction is lower than in LDPE by a factor 1.2–1.4. The miscibility of XN in PP is supposed to be higher than in LDPE since almost no XN sweating was observed from PP containing 0.3% XN. Thus, the most probable reason for a low efficiency of PP crosslinking is the ability of preferentially formed tertiary-alkyl macroradicals to  $\beta$ -scission.<sup>14-18,23</sup>

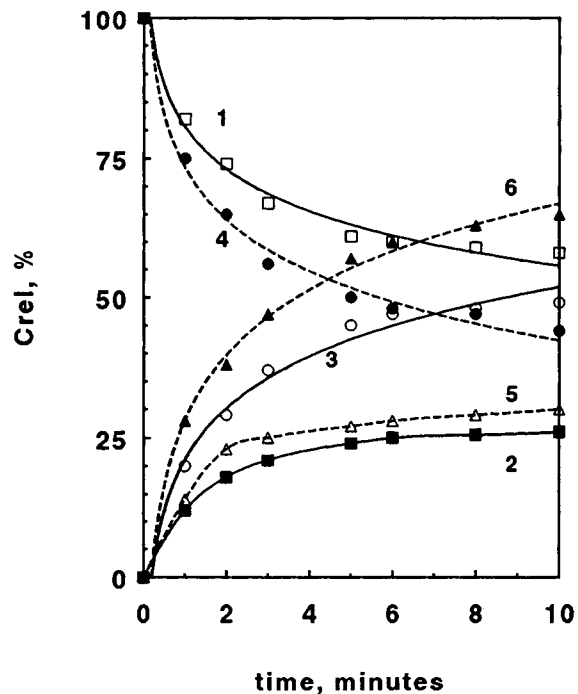


**Figure 4** Gel content in PP vs. irradiation time; photocrosslinking initiated by XN at (1) 30 or (3) 170°C and by XN in the presence of TAC at (2) 30 or (4) 170°C.

The rate of TAC photografting and allyl group conversion in PP was found to be only slightly lower than in LDPE at 30°C (Fig. 5), but the  $n$  value mainly stays close to 1 and exceeds unity only at the beginning of UV exposition (Fig. 3). Thus, the anchoring of grafted chains to the other macromolecules (reactions 8 and 13) in PP is less effective than in LDPE. In comparing the data shown in Figures 2 and 5, it may be seen that more allyl groups remain intact in TAC-grafted chains in PP than in LDPE. For example, after extraction of LDPE foils irradiated for 3 min at 30°C, the IR absorption intensities were found to be 62 and 24% of the initial values, respectively (Fig. 2). These data lead to an estimation that 61% of the originally added TAC molecules were grafted and the average number of consumed and intact allyl bonds per TAC molecule are 1.8 and 1.2, respectively. In PP after the same irradiation procedure, the portions of TAC grafted and unreacted allyl groups were found to be 38 and 20% of the initial values, respectively (Fig. 5), i.e., only 1.4 allyl groups were consumed per one TAC molecule. Correspondingly, the higher branching of grafts in LDPE can be attributed to more efficient anchoring of macroradicals to TAC grafts and formation of multifunctional junctions.

A not too surprising feature is that at short UV-irradiation periods the experimentally determined number of consumed TAC allyl groups is higher than that estimated from the portion of TAC grafting and the average number of reacted groups in the grafts. This difference indicates that some allyl groups are consumed in the process of a formation of the extractable oligomer (reaction 14). Under given irradiation conditions, the portion of the allyl bonds consumed for grafting is  $(1.8 \times 61)/3 = 36.6\%$  in LDPE and  $(1.4 \times 38)/3 = 17.7\%$  in PP. Since the corresponding experimental values were determined to be 40% for LDPE (Fig. 2) and 31% for PP (Fig. 5), the portion of TAC moieties consumed in the parasitic reaction of oligomer formation would be 3.4 and 13.3% in LDPE and PP, respectively. Prolonged irradiation was found to result in a decrease of the portion of soluble products containing TAC, although the amount of the latter was always higher in PP than in LDPE.

The difference between LDPE and PP regarding TAC effectivity in photocrosslinking increases with temperature. Taking the UV-exposition time of 3 min for LDPE at 170°C, the TAC content in LDPE

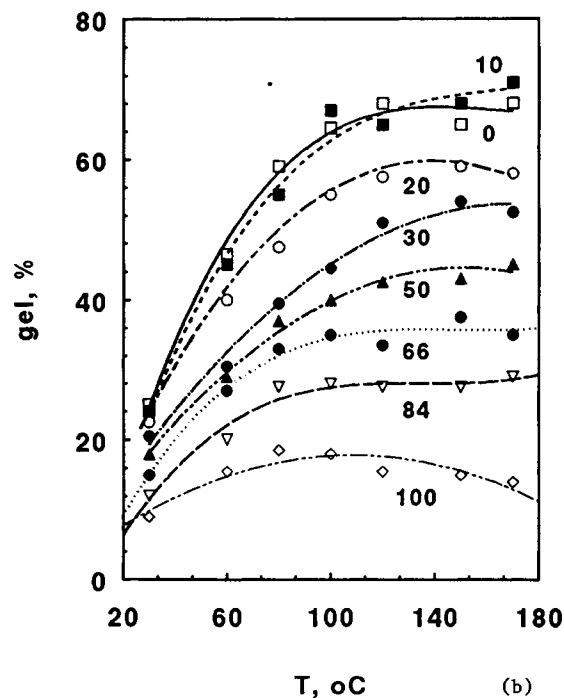
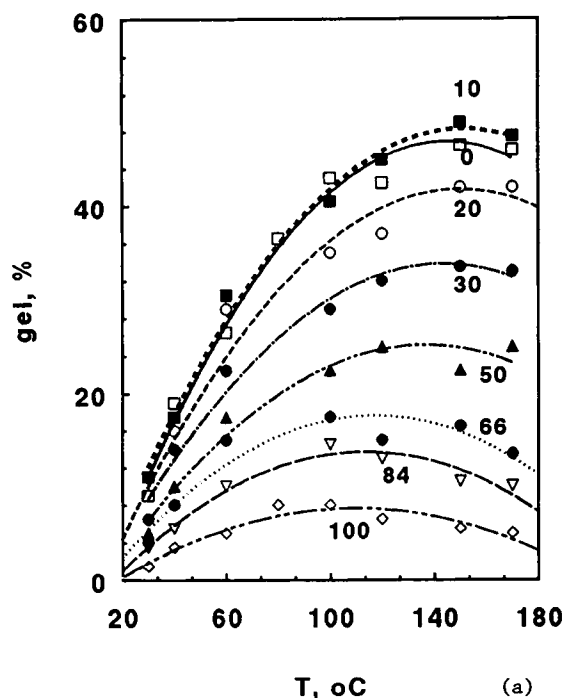


**Figure 5** The dependence of relative concentration of (1, 4) intact TAC allyl double bonds, (2, 5) unreacted allyl double bonds, and (3, 6) grafted triazine groups in extracted photocrosslinked PP films. The temperature for UV-light exposition was 30 (full line) and 170°C (dotted line).

was determined to be 85% of the initial amount, with only 13% of the allyl groups intact from the total amount (Fig. 2), while in PP, the corresponding values are 47 and 23%, respectively (Fig. 5). Thus, the average number of consumed allyl groups per one grafted TAC molecule is 2.5 in LDPE and 1.5 in PP, the ratio of these two values being higher than the same ratio at room temperature. A low ratio between TAC molecules grafted to PP and the number of grafting sites found in the melt is also confirmed by low  $n$  values (Fig. 3). This observation correlates with a substantial increase of gel yield in LDPE and an opposite result for PP (Figs. 1 and 4) if the samples were crosslinked above the melting temperature.

To explain a different effect of TAC in PE and PP, it is necessary to remember that grafting and recombination reactions compete with degradation of tertiary-alkyl radicals in PP. Since two low mobile macroradicals have to meet for crosslinking and only one macroradical and low molecular weight substance for grafting, the latter reaction could compete more successfully with monomolecular scission. This assumption is supported by the data of peroxide-induced grafting in ethylene-propylene copolymers.<sup>34</sup> However, the main TAC effect in network formation consists of successive anchoring of different macroradicals to TAC grafts through reactions 8 and 13. These reactions ought to be dependent on the macroradical mobility. If the latter is too low, the termination can occur by chain-transfer reactions with TAC molecules, resulting in TAC oligomer formation. This appears to be the main reason why in PP where macroradicals are less mobile than in LDPE<sup>31</sup> linear TAC grafts are mainly formed, the yield of oligomers is quite high, and crosslinking is not substantially enhanced. It correlates with the fact that the grafting of bulky molecules initiated by peroxide<sup>31</sup> or photochemically<sup>35,36</sup> is more efficient in LDPE than in PP.

Since the temperature appears to be a very significant parameter in both LDPE and PP photocrosslinking, the temperature effect was investigated in LDPE/PP blends at various compositions. The plots of gel formation vs. UV-exposition time in blends are similar to those in LDPE (Fig. 1), but differ by an induction period of gel formation, slope on the steep part of the curve, and maximal attainable level of gel content. Some deviations were found only in PP-rich blends photocrosslinked at elevated temperatures. For these samples, gel vs. time plots decrease after attaining the maximal gel content, similarly to the course of dependence in the PP melt (Fig. 4). The influence of temperature may be illus-

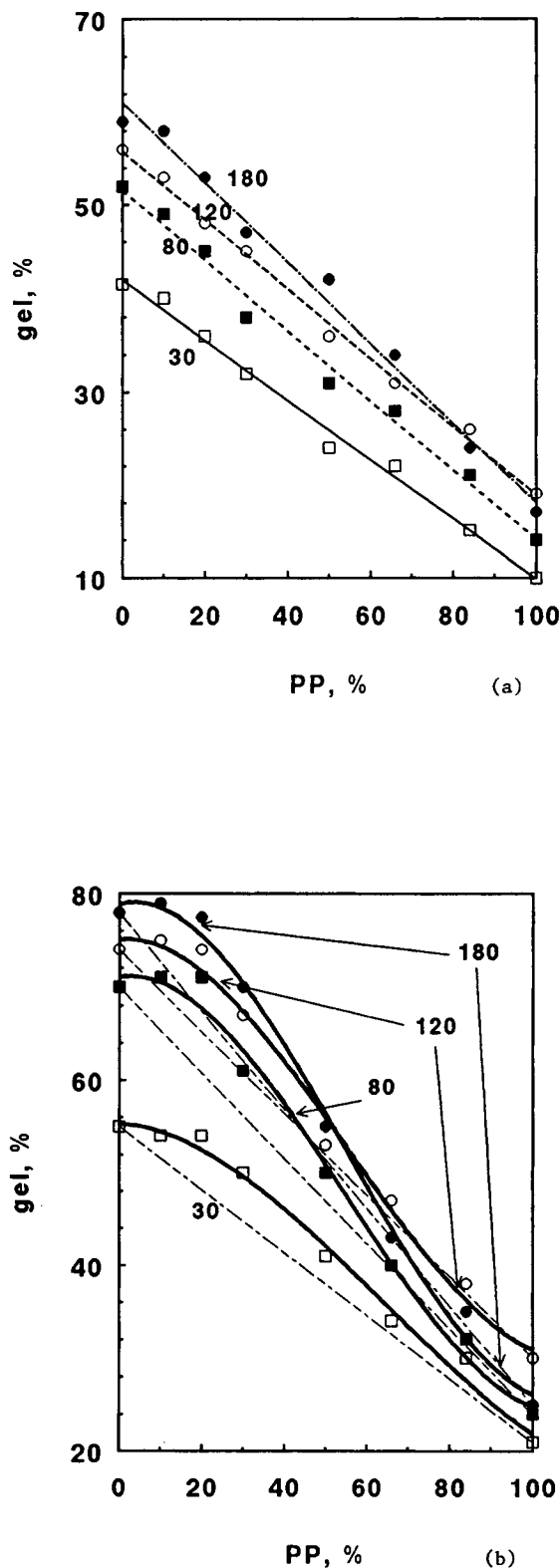


**Figure 6** Effect of UV-irradiation temperature on the gel output in LDPE/PP blends in the presence of (a) XN or (b) XN and TAC. PP content (%) is indicated by the numbers at the curves. Irradiation time 1 min.

trated, presenting gel outputs in different blends at constant UV-irradiation time in the steep part for all the correspondent curves [Fig. 6(a) and (b)]. Apparently, photocrosslinking efficiency increases substantially with a temperature increase up to 100–120°C for all blends. Further temperature growth results in a less pronounced enhancement of crosslinking for most blends. However, in PP and in blends containing 66 and 84% of PP which were crosslinked without a coagent, the temperature increase above 120°C leads to the opposite effect. Thus, the maximal photocrosslinking effectiveness for these blends is observed in the temperature interval 80–120°C. If TAC is used as a coagent, the gel content grows with temperature up to 170°C in all blends [Fig. 6(b)].

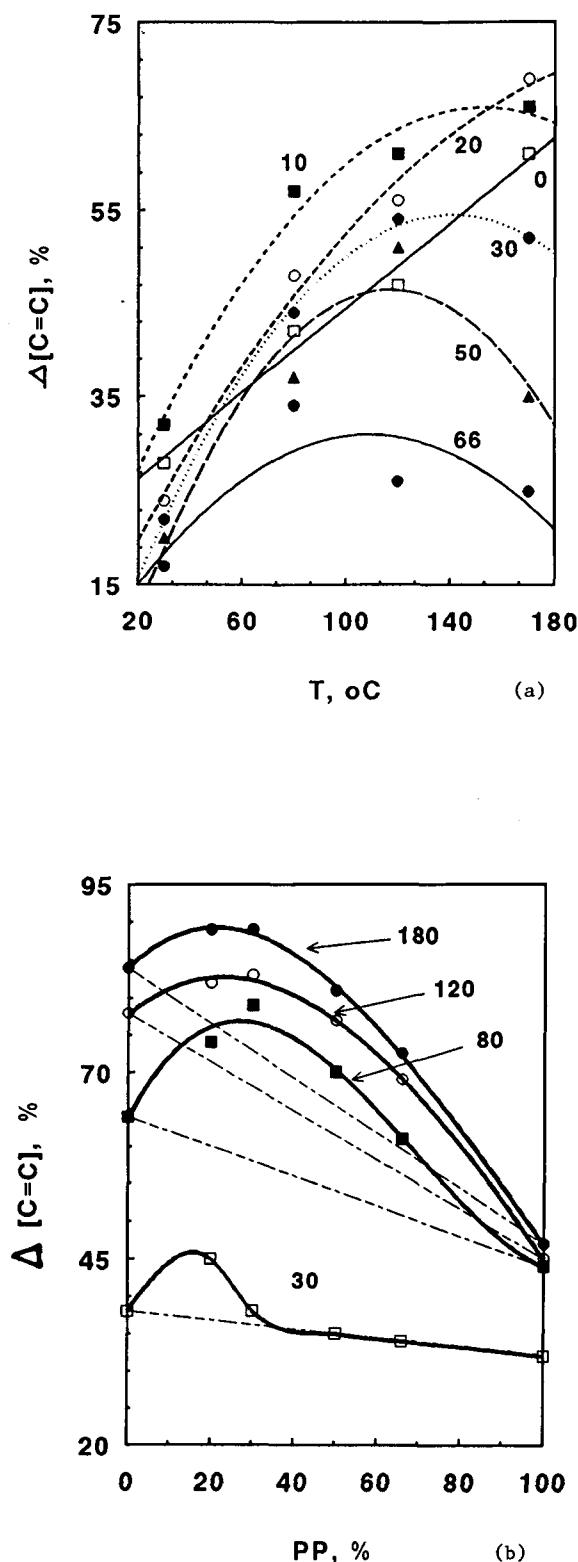
The amount of the gel formed decreases with increasing PP content. The plots of gel vs. composition hardly change the shape with varying temperature in the blends photocrosslinked with XN both in the presence or absence of TAC [Fig. 7(a) and (b)]. When photocrosslinking of blends proceeds in an absence of a coagent, the experimental data for various compositions closely follow the additivity curve [Fig. 7(a)]. If crosslinking occurs in the presence of TAC, the experimental results for gel output were found to be slightly above the additive values for the compositions containing from 10 to 30 and 84% PP [Fig. 7(b)]. More significant deviations from the additivity were found for the TAC allyl double-bond conversion if the blends were heated above 80°C during UV-light exposition [Fig. 8(a)]. Maximal TAC allyl group conversion was achieved in the compositions containing 20 or 30% of PP. Temperature dependencies for TAC allyl group conversion after a shorter exposition [Fig. 8(b)] show the same tendency: The yields increase with temperature, except in PP, where maxima were observed at 80°C.

The intensity of the incident light is another valuable parameter of UV irradiation. UV-light intensity decreased by approximately one order of magnitude using calibrated nets placed between the light source and the sample. It is assumed that the reactions of xanthone do not depend on the light intensity within this interval<sup>19,21</sup> and are only controlled by the amount of absorbed quanta, which may be characterized by multiplying the relative intensity of the incident light ( $I_x$ ) by the exposition time ( $t_x$ ). The conversions of gel output and TAC allyl groups vs.  $I_x t_x$  are plotted in Figure 9 for the blends containing 20 and 66% of PP. These measurements showed that in spite of some scatter in the experimental results a master curve can be constructed for each blend at different  $I_x$  but for the



**Figure 7** Plots of the gel output vs. PP content in the blends containing (a) XN or (b) XN and TAC. Temperature of irradiation (°C) indicated by the number at the curve.





**Figure 8** Conversion of TAC allyl groups vs. (a) temperature after 1 min of UV-irradiation (PP content in % given by the number at the curve) and vs. (b) PP content in blends (temperature of irradiation indicated by the number at the curve) after 3 min of UV irradiation.

same  $I_x t_x$ . The increase of temperature from 30 to 170°C enhances the output of photoinitiated processes in LDPE/PP blends but does not reveal any change in the character of light-intensity influence. Since these results correlate with the data previously obtained for LDPE containing TAC,<sup>19</sup> we can conclude that the composition has no effect on the almost proportional dependence of the crosslinking yield and TAC allyl group conversion on  $I_x$ .

The deviation of the gel output and TAC allyl group conversion from the additive values [Figs. 7(b) and 8(a) and (b)] may raise a question about the interaction between the components in the blend in photoinitiated processes and the distribution of junctions. Some information on this topic could be obtained from the data of consecutive extraction of crosslinked blends in boiling cyclohexane and boiling xylene. During the extraction in cyclohexane, PE sol is dissolved while the uncrosslinked PP part remains mostly insoluble. This portion is extracted afterward in boiling xylene.

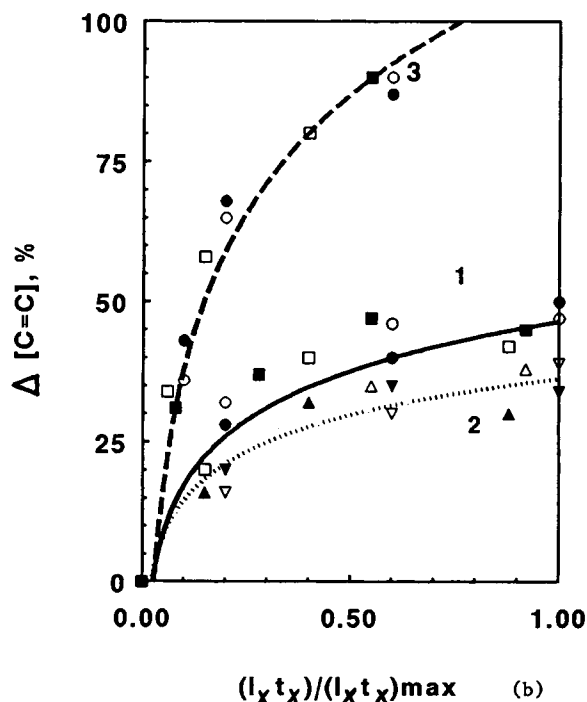
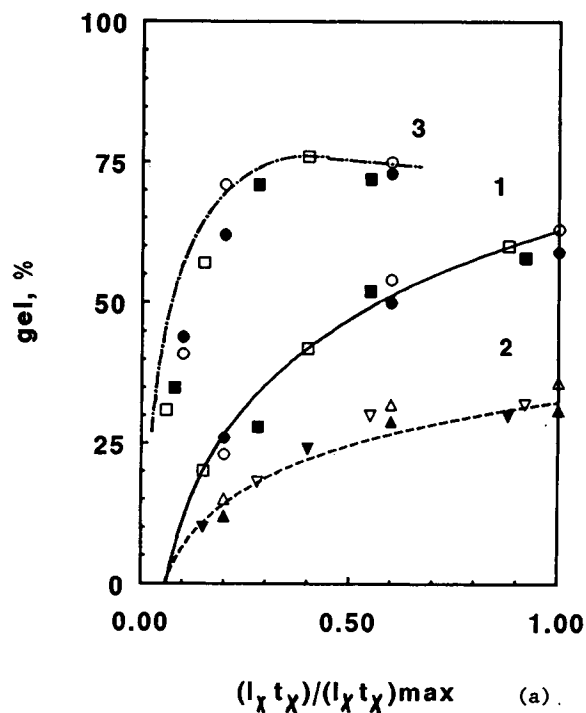
It was shown previously that the PE sol fraction can be successfully removed from peroxy crosslinked PE/PP blends by boiling cyclohexane, but some cyclohexane soluble PP fractions have also been formed.<sup>14</sup> This effect is ascribed to the PP degradation accompanying the crosslinking initiated by peroxides. We made this consecutive extraction procedure using uncrosslinked blends and photocrosslinked PP and LPDE. It was found that after the extraction of uncrosslinked samples in boiling cyclohexane the weight of the insoluble portion is almost equal to the PP portion in the blend. Extraction of photocrosslinked homopolymers showed the same trends as in peroxide crosslinked samples.

In LDPE, nearly all the sol fraction is extracted by cyclohexane while the solubility of PP is very limited (3–6%), increasing with UV-irradiation time. For example, from PP samples in which 17% of gel was determined according to extraction in xylene, 14% of initial weight was dissolved in cyclohexane. Considering the photocrosslinking and degradation of LDPE and PP phases as independent processes, the insoluble part after the sample extraction in cyclohexane ( $g_{\text{cycl}}$ ) should be equal to a value calculated from extraction data according to equation

$$g_{\text{cycl}} = \frac{m_{\text{PP}}}{m_{\text{LDPE}} - m_{\text{PP}}} (g_{\text{cycl}}^{\text{PP}} - g_{\text{xyl}}^{\text{PP}}) + g_{\text{xyl}} \quad (2)$$

which could be rearranged to

$$g_{\text{cycl}} - g_{\text{xyl}} = \frac{m_{\text{PP}}}{m_{\text{LDPE}} - m_{\text{PP}}} (g_{\text{cycl}}^{\text{PP}} - g_{\text{xyl}}^{\text{PP}}) \quad (3)$$



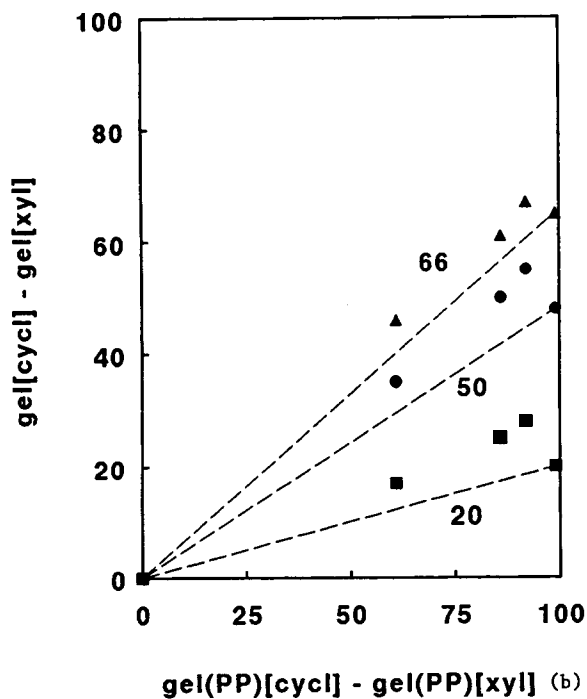
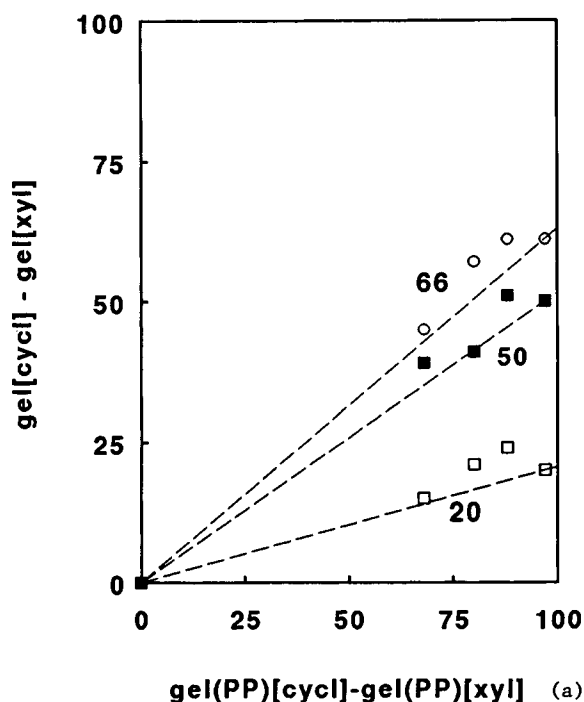
**Figure 9** (a) Gel output and (b) TAC allyl groups conversion vs. relative incident irradiation dose at (1, 2) 30 and (3) 170°C in the blends containing (1, 3) 20 and 66% of PP; the relative incident light intensities are (○, △) 1.0, (●, ▼) 0.435, (■, ▽) 0.265, and (□, ▲) 0.115.

where  $m_{PP}$  and  $m_{LDPE}$  are the weight portions of respective polymers in the blend;  $g_{xyl}$  is the gel content in the sample after boiling in xylene; and  $g_{cycl}^{PP}$  and  $g_{xyl}^{PP}$  are the insoluble portions of PP as the reference sample after its irradiation for the same time and boiling in cyclohexane and in xylene, consecutively.

In Figure 10(a) and (b), the plot of  $g_{cycl} - g_{xyl}$  vs.  $g_{cycl}^{PP} - g_{xyl}^{PP}$  is constructed according to Eq. (3) for the blends containing 66, 50, and 20% of PP when photocrosslinked with XN in either the presence or absence of TAC. The deviation of experimental data from the theoretical fit is obvious at low irradiation time, especially if photocrosslinking proceeds in the presence of TAC. At high gel content, the deviation is smaller and approaches zero for the XN photocrosslinked samples without TAC. It is of interest that the most substantial deviation is observed for the composition containing 20% of PP. The most reasonable interpretation of these results is that at the beginning of irradiation some LDPE molecules are attached by a chemical bond to the interface of the PP phase which, although insoluble in cyclohexane, is not included in the network yet and can be dissolved in xylene. The amount of the cyclohexane insoluble part increases in the same way and the deviation of experimental results from the values predicted by Eq. (3) is observed. This deviation was suppressed by further crosslinking because the grafted molecules have been attached to the network formed in both phases.

It should be pointed out that the positive deviation of the gel output and conversion of TAC allyl groups from the additive dependence in LDPE/PP blends as well as the results on the samples' solubility in cyclohexane and xylene cannot be attributed to the preferential sorption of photoinitiator in one of the phase.

None of these deviations were observed in the blends containing 50 or 66% of PP or in the phase transition region.<sup>7,8</sup> In that case, the volume of dispersed particles increased and a semicontinuous microphase could be formed. Therefore, a lower number of LDPE and PP chains are present at the interface when compared to the blends with a lower content of the minor component. Preferential sorption and reactions of TAC in the interface region could contribute to interpolymer crosslinking of LDPE and PP chains. The increase of concentration of TAC allyl double bonds in the boundary region can increase the rate of its conversion more in compositions containing 20–30% of PP higher than in LDPE.



**Figure 10** The dependence according to Eq. (3) for LDPE/PP blends containing (a) XN or (b) XN and TAC. PP content in the blend (%) is given by the number at the curve; temperature of irradiation, 80°C.

## CONCLUSIONS

It was shown that photocrosslinking efficiency for LDPE/PP blends is substantially increased in the presence of triallyl cyanurate as a coagent and the mechanism of the TAC action is proposed. The level of photocrosslinking efficiency in PP is lower than that in PE and decreases with increasing PP content in the LDPE/PP blends.

For all investigated materials, both the crosslinking degree and TAC allyl group conversion is enhanced with increasing UV-irradiation temperature and the rate of these reactions is almost proportional to incident UV-light intensity. Indirect evidence for the formation of polyethylene-polypropylene links in the interfacial region were obtained in the blends photocrosslinked in the presence of TAC.

## REFERENCES

1. J. W. Teh, *J. Appl. Polym. Sci.*, **28**, 605 (1983).
2. J. Kolařík, G. L. Agrawal, Z. Kruliš, and J. Kovář, *Polym. Compos.*, **7**, 463 (1986).
3. V. Flaris and Z. H. Stachurski, *J. Appl. Polym. Sci.*, **45**, 1789 (1992).
4. M. Levij and F. H. J. Maurer, *Polym. Eng. Sci.*, **28**, 670 (1988).
5. I. Chodak, *Macromol. Chem. Macromol. Symp.*, **41**, 229 (1991).
6. P. Cheung, D. Suwanda, and S. T. Balke, *Polym. Eng. Sci.*, **30**, 1063 (1990).
7. W. Chiu and S. Fang, *J. Appl. Polym. Sci.*, **30**, 1473 (1985).
8. M. M. Dumoulin, C. Furha, and L. A. Utracki, *Polym. Eng. Sci.*, **24**, 1319 (1984).
9. H. W. Starweather, F. A. Van-Catledge, and R. N. McDonald, *Macromolecules*, **15**, 1600 (1982).
10. F. Eirich, *J. Appl. Polym. Sci.*, **39**, 93 (1984).
11. L. Minkova and N. Nikolova, *Polym. Degrad. Stab.*, **23**, 217 (1989).
12. G. Rizzo, G. Spadaro, D. Acierno, and E. Calderaro, *Radiat. Phys. Chem.*, **21**, 349 (1983).
13. D. Kostoski and Z. Kacarovic-Popovic, *Polym. Commun.*, **29**, 142 (1988).
14. E. Borsig, A. Fiedlerova, L. Rychlá, M. Lazár, G. Haudel, and M. Rätzsch, *J. Appl. Polym. Sci.*, **37**, 467 (1989).
15. I. Chodak, I. Janigova, and A. Romanov, *Macromol. Chem.*, **192**, 2791 (1991).
16. T. Sasuga, S. Kavanishi, M. Nishii, T. Seguchi, and I. Kohno, *Radiat. Phys. Chem.*, **37**, 673 (1991).
17. L. M. Plotnikov and J. Reskens, *Vysokomol. Soed.*, **B28**, 89 (1986).
18. S. Nashimoto, K. Kitamura, Y. Watanabe, and T. Kagiya, *Radiat. Phys. Chem.*, **37**, 71 (1991).

19. P. Zamotaev and O. Mityukhin, *Vysokomol. Soed. A*, **35**, 413 (1993).
20. Y. L. Chen and B. Ranby, *J. Polym. Sci. Polym. Chem.*, **27**, 4051 (1989).
21. P. V. Zamotaev, *Makromol. Chem. Makromol. Symp.*, **28**, 287 (1989).
22. C. Sadmohaghegh, G. Scott, and E. Setoudeh, *Polym. Degrad. Stab.*, **3**, 469 (1980–81).
23. N. Grassie and W. B. H. Leeming, ACS Symposium Series 25, American Chemical Society, Washington, DC, 1976, p. 367.
24. E. V. Lebedev, in *Physico-chemistry of Multi-component Polymer System*, J. Lipatov, Ed. Nauk. Dumka, Kiev, 1986, Vol. 2, p. 74.
25. J. K. Gillham and C. C. Mentzer, *J. Appl. Polym. Sci.*, **17**, 1143 (1973).
26. W. K. Bushfield, *Eur. Polym. J.*, **17**, 333 (1981).
27. V. I. Dakin, A. V. Danchenko, and V. L. Karpov, *Vysokomol. Soed. A*, **26**, 2211 (1984).
28. W. Gentzkov and H. Markert, *Siemens Forsch. Entwickl. Ber.*, **16**, 90 (1987).
29. V. K. Milinchuk, A. R. Klinshpont, and S. Ja. Pshedzhetskii, *Macroradicals*, Chemistry Ed., Moscow, 1980, p. 264.
30. V. M. Dakin, Z. S. Egorova, and V. L. Karpov, *Vysokomol. Soed. A*, **23**, 2727 (1981).
31. Y. N. Sharma, M. K. Naqvi, P. S. Gavande, and I. S. Bhardwaj, *J. Appl. Polym. Sci.*, **27**, 2605 (1982).
32. I. Chodák and I. Chorváth, unpublished results.
33. I. Chodák and L. Rychlá, in *Proceedings of the International Conference Advances in Stabilization*, Luzern, May 1990.
34. R. Greco, G. Maglio, P. Musto, and G. Scarinzi, *J. Appl. Polym. Sci.*, **37**, 777 (1989).
35. P. V. Zamotaev and O. P. Mityukhin, *DAN Ukraine*, **9**, 125 (1992).
36. K. Allmer, A. Hult, and B. Ranby, *J. Polym. Sci. Polym. Chem.*, **27**, 3405 (1989).

Received December 29, 1993

Accepted October 15, 1994