

Thermal and Mechanical Properties of Poly(ϵ -caprolactone) Crosslinked with γ Radiation in the Presence of Triallyl Isocyanurate

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Received 6 December 2005; accepted 19 June 2006

DOI 10.1002/app.25419

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Poly(ϵ -caprolactone) was crosslinked by γ radiation in the presence of triallyl isocyanurate. The influence of γ -radiation crosslinking on the thermal and mechanical properties of poly(ϵ -caprolactone)/triallyl isocyanurate was investigated. Differential scanning calorimetry analyses showed differences between the first and second scans. Dynamic mechanical analysis showed an increase in the glass-transition temperature as a result of the radiation crosslinking of poly(ϵ -caprolactone). Thermogravimetric analysis showed that γ -radiation crosslinking slightly improved the thermal stability of poly(ϵ -caprolactone). The γ radiation also strongly influenced the mechanical properties. At room temperature, crosslinking by radiation did not have a signifi-

cant influence on the Young's modulus and yield stress of poly(ϵ -caprolactone). However, the tensile strength at break and the elongation at break generally decreased with an increase in the crosslinking level. When the temperature was increased above the melting point, the tensile strength at break, elongation at break, and Young's modulus of poly(ϵ -caprolactone) were also reduced with an increase in the crosslinking level. The yield stress disappeared as a result of the disappearance of the crystallites. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2676–2681, 2007

Key words: biodegradable; crosslinking; mechanical properties; polyesters; radiation; thermal properties

INTRODUCTION

There is growing interest in developing biodegradable polymers to replace synthetic nonbiodegradable materials. Aliphatic polyesters, such as polylactide, poly(3-hydroxybutyrate), and poly(ϵ -caprolactone) (PCL), represent a useful range of biodegradable polymers that can be used to alleviate waste-disposal problems.^{1–3} In the family of polyesters, PCL (Scheme 1), derived from the ring-opening polymerization of ϵ -caprolactone, is considered an ideal biodegradable polymer and has recently received much attention because of its flexibility and good biodegradability.^{4–8} Additionally, like other aliphatic polyesters such as polylactide and polyglycolide, PCL and its copolymers have commercially successful applications.^{9,10} PCL has, however, been restricted in its applications because of its low melting temperature (T_m), poor stability, and tendency to rack when stressed.¹¹ In an effort to tackle these disadvantages, there has been considerable work based on the crosslinking of PCL. By the introduction of crosslinks into PCL, physical

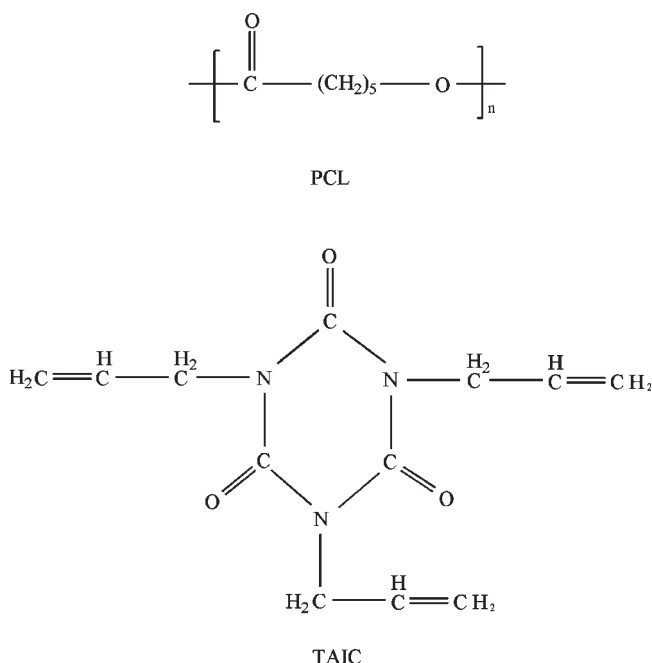
properties such as the degree of crystallinity (X_c) and T_m will be influenced. The characteristics of degradation by hydrolysis will in turn also be influenced. Certain mechanical properties, such as the creep resistance and high-temperature dimensional stability, are in general improved by crosslinking. These properties are very important in applications. Furthermore, the modulus, tensile strength, and elongation at break of the polymer will be affected by crosslinking, either directly or indirectly.¹²

Radiation is a very convenient method for the improvement of polymeric materials by crosslinking, grafting, and degradation.^{13–15} The molecular changes, induced by radiation, in a polymer can be classified as main-chain bond scission, resulting in a decrease in the molecular weight and thus adversely affecting its mechanical properties, and chain crosslinking, resulting in an increase in the molecular weight and the formation of a network structure. Both chain scission and crosslinking occur primarily in the amorphous region, with some taking place in the interphase between the crystalline and amorphous regions. It must be emphasized that the two mechanisms, that is, chain scission and crosslinking, depend on the radiation dose, the radiation temperature, the type of polymer, the radiation medium, and the added coupling agent. Chain scission has been shown to occur in polymers at high radiation doses.

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Contract grant sponsor: National Science Foundation of China; contract grant number: 50473028.

Journal of Applied Polymer Science, Vol. 103, 2676–2681 (2007)
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Scheme 1 Chemical structures of PCL and TAIC.

At temperatures below the glass-transition temperature (T_g), crosslinking is retarded because of the lower chain mobility, whereas at temperature above T_g , the crosslinking rate increases significantly with increased chain mobility.¹⁴ The structure and some physical properties of irradiated PCL have been investigated by many authors. Narkis et al.¹⁶ studied the structure and physical properties of γ -irradiated PCL as a function of the irradiation dose level. Studied doses of up to 70 Mrad caused gel contents of about 35% in PCL. Darwis et al.¹⁷ found that the dose required for crosslinking PCL depended on the state of the irradiated polymer: it was relatively low when the polymer was irradiated in the molten or supercooled state. Moreover, crosslinked PCL was also achieved by electron-beam irradiation in the presence of polyfunctional monomers.¹⁸ Triallyl isocyanurate (TAIC) has been used in industry as a crosslinking agent for polyolefin and vinyl polymers¹⁹ and recently was reported to be an effective crosslinking agent for polylactide^{20,21} and poly(butylenes succinate).²² In this study, PCL was crosslinked by radiation in the presence of TAIC. Thermal properties such as T_m , X_c , T_g , and the thermal stability were examined. Finally, the mechanical properties of control and crosslinked PCLs and their dependence on the gel fraction and temperature were investigated.

EXPERIMENTAL

PCL was a commercial product (CAPA6500, Solvay Interlox, Ltd., Cheshire, UK). TAIC was purchased from Aldrich and used as received.

TAIC was blended with PCL in an internal mixer (Rheomix 600p, Haake, Karlsruhe, Germany) at 110°C and 50 rpm for 5 min. Then, the samples were hot-pressed at 130°C for 3 min and then cold-pressed at room temperature to form films 1 mm thick. For comparison, pure PCL was treated with the same procedure.

Each film sample was heat-sealed in a polyethylene bag *in vacuo* and then irradiated by γ rays (10 kGy/h) from a ⁶⁰Co source with various radiation doses.

The gel content of the crosslinked PCL was determined gravimetrically with a Soxhlet extraction cycle with boiling chloroform as the solvent for 72 h. Approximately 0.2 g of the crosslinked polymer sample was cut into small pieces and placed in a preweighed, stainless steel, fine mesh. After the extraction, the samples were washed with acetone and vacuum-dried to a constant weight. The gel fraction was calculated as follows:

$$\text{Gel fraction} = (W_2/W_1) \times 100\% \quad (1)$$

where W_1 is the initial weight of the sample and W_2 is the weight of the sample after extraction.

Thermogravimetric analysis (TGA) was carried out on a PerkinElmer TGA7 thermal analyzer (Wellesley, MA) from 35 to 600°C at a heating rate of 10°C/min in a nitrogen atmosphere. Differential scanning calorimetry (DSC) was carried out on a PerkinElmer DSC7 thermal analyzer in a nitrogen atmosphere. The samples were heated from -50 to 100°C at a heating rate of 10°C/min and then cooled at the same rate. Thermal properties, such as T_m and the melting enthalpy, were determined from both the first and second scans.

Dynamic mechanical analysis (DMA) was carried out with a Netzsch 242 dynamic mechanical analyzer (Netzsch, Germany) in a single-cantilever mode. Specimens with dimensions of 30 × 10 × 1 mm³ were used. The samples were heated from -100 to 0°C at a heating rate of 3°C/min and at a frequency of 1 Hz.

For the determination of the mechanical properties, an Instron 1211 testing machine (Norwood, MA) was used. The test was carried out with a crosshead speed of 100 mm/min at two temperatures, 25 (room temperature) and 70°C ($>T_m$). The reported values are averages of at least five dumbbell-shaped specimens with necks 20 mm long and cross-sectional areas of 4 × 1 mm².

RESULTS AND DISCUSSION

Gel fraction determination

Introducing a few percent of TAIC as a crosslinking agent into the PCL samples led to the formation of a gel even at the low absorbed dose of 10 kGy (Fig. 1).

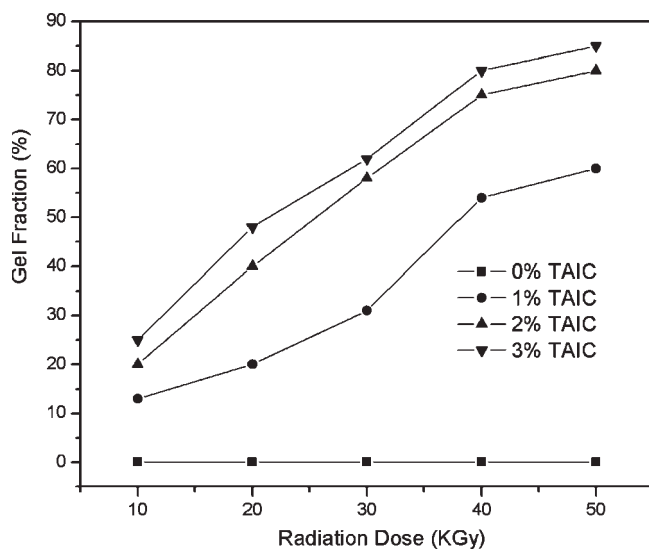


Figure 1 Gel fraction of PCL as a function of the radiation dose at different concentrations of TAIC.

A high gel fraction of 85% was obtained in the sample containing 3% TAIC at a dose of 50 kGy, whereas the irradiated samples without TAIC completely dissolved in the solvent within the absorption dose range of 10–50 kGy. At a definite TAIC level, the extent of gel formation increased with an increase in the absorbed dose up to 40 kGy and then seemed to remain nearly constant, as shown in Figure 1. Increasing the percentage of the crosslinking agent introduced more active sites into the system, and this led to the formation of a tighter network with a higher degree of crosslink density at a given absorbed dose.

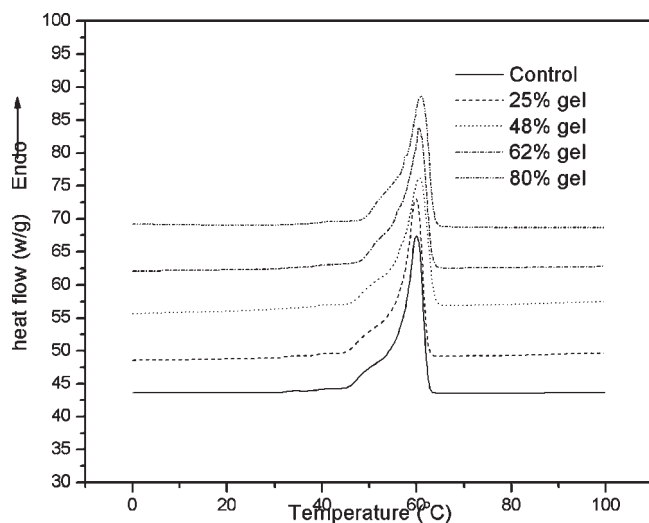


Figure 2 First scan of a DSC diagram of control and crosslinked PCLs containing 3% TAIC and different gel contents.

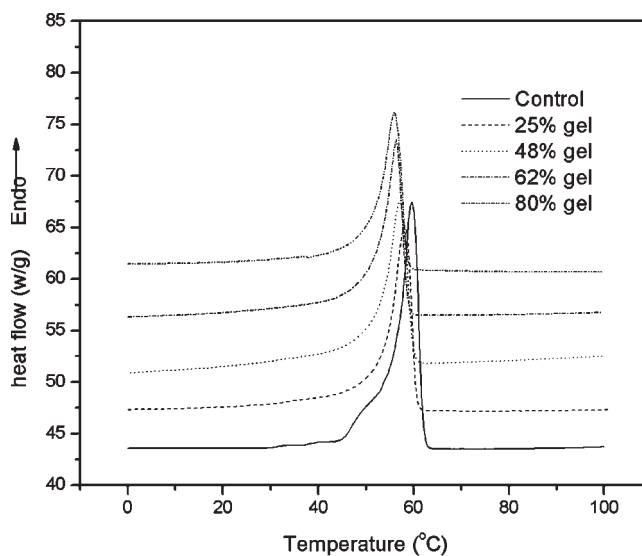


Figure 3 Second scan of a DSC diagram of control and crosslinked PCLs containing 3% TAIC and different gel contents.

DSC

Figures 2 and 3 show the first and second scans of DSC for control and irradiated PCL samples, respectively. T_m (determined as the peak temperature), the heat of fusion [i.e., the specific enthalpy of melting (ΔH_m)], and X_c , as determined from DSC measurements, for control and crosslinked PCLs with different gel contents are summarized in Table I. X_c has been calculated via the total enthalpy method according to the following equation: $X_c = \Delta H_m / \Delta H_m^+$, where ΔH_m^+ is the specific enthalpy of melting for 100% crystalline PCL (136 J/g according to the literature²³). The principal differences between the first and second scans can be clearly seen. From the first scan, it is evident that crosslinking has no significant influence on T_m and X_c . This is due to the fact that the crosslinking occurs well below T_m under radiation conditions. The radiation crosslinking occurs predominantly in the amorphous regions, so it is reasonable to expect T_m and X_c , as measured during the first scan, to not change with increasing crosslinking. Conversely, the fact that T_m and X_c for the radiation-crosslinked samples have not changed can be taken as an indication that the crystalline regions are hardly crosslinked in this process. For the second scan, however, T_m and X_c decrease with the extent of crosslinking. The reason for this decrease is that, in the second scan, the PCL samples were recrystallized in the presence of crosslinks. During the recrystallization process, crosslinks that form between polymer chains act as defect centers, which restrict chain mobility and hinder the folding and packing of PCL chains. Thus, a higher extent of crosslinking should yield progressively lower T_m .

TABLE I
 T_m , ΔH_m , and X_c Values of Control and Crosslinked PCLs with 3% TAIC and Different Radiation Doses

Dose (kGy)	Gel fraction (%)	First run			Second run		
		T_m ($^{\circ}$ C)	ΔH_m (J/g)	X_c (%)	T_m ($^{\circ}$ C)	ΔH_m (J/g)	X_c (%)
0	0	60.1	70.5	51.8	59.7	70.3	51.7
10	25	60.0	71.6	52.6	58.0	66.0	48.5
20	48	60.8	68.4	50.3	56.9	61.8	45.4
30	62	60.4	70.3	51.7	56.4	58.4	42.9
40	80	60.8	69.1	50.8	56.0	53.0	39.0

and X_c materials, and this is what is shown in Figure 3 and Table I.

Dynamic T_g

Dynamic mechanical studies provide very sensitive means of determining the transition behavior of polymers. According to the literature,²⁴ DMA of PCL before melting reveals two transitions. The two transitions correspond to different motions in PCL chains. The low-temperature transition occurring in the range of -150 to -100° C is due to the motion in the amorphous regions of segments of the chains comprising three or more methylene units. The transition occurring near the temperature of about -60° C is considered T_g , and as discussed here, the influence of the physicochemical parameters on this transition can be explained in terms of T_g . Figures 4 and 5 show the storage modulus and $\tan \delta$ versus the temperature for control and crosslinked PCLs with 80% gel. The temperature at which a sharp drop in the storage modulus and the maximum of $\tan \delta$ occur increases with an increase in the gel content. Compared with T_g of the control, T_g of crosslinked PCL increases after crosslinking. This could be due to the fact that in radiation crosslinking,

because exposure occurs in the solid state, the crystalline phase does not undergo any changes (see Fig. 1); instead, the crosslinking takes place only in the amorphous phase. This restricts the segment mobility of the polymer chains. The restrictions on the motion of the segment of PCL in the amorphous phase increase the energy requirements for the transition and thereby raise T_g . A similar shift in T_g to a higher temperature with the radiation crosslinking of poly(butylenes succinate) in the presence of TAIC was also reported by Suhartini et al.²²

Decomposition temperature

Figure 6 shows TGA curves for control and crosslinked PCL samples with various gel contents. PCL decomposes completely in a single stage, beginning at about 340° C, and does not show a major weight loss up to about 400° C, beyond which a sharp weight loss can be observed, as reported by Corradini et al.²⁵ This behavior is almost identical for all the samples, although there is a slight increasing trend in the onset of the thermal decomposition with an increase in the gel fraction. The formation of more compact three-dimensional structures can improve thermal stability because they are more stable

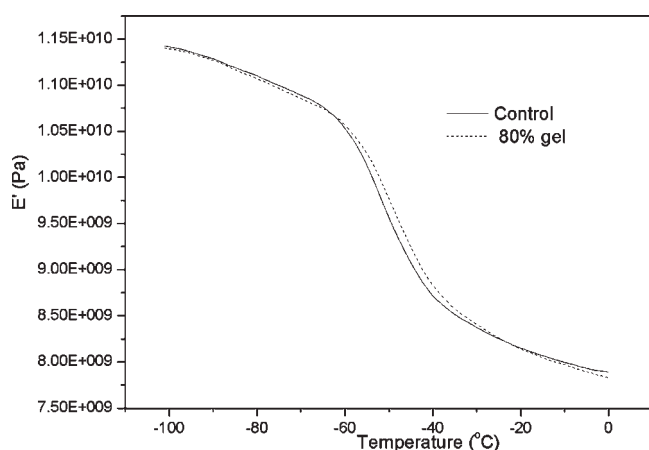


Figure 4 Effect of crosslinking on the storage modulus (E') of PCL.

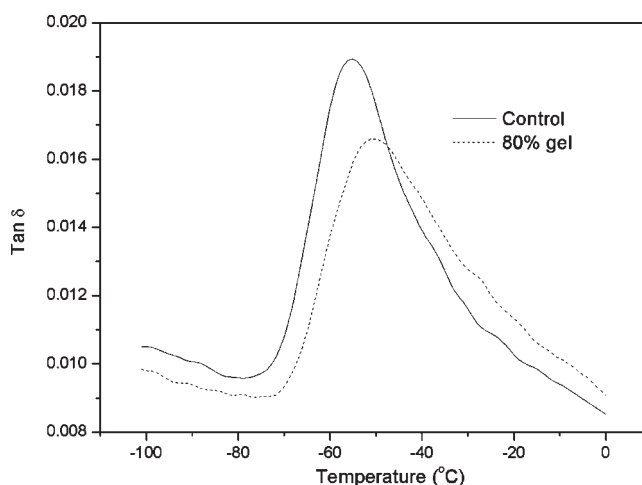


Figure 5 Effect of crosslinking on $\tan \delta$ of PCL.

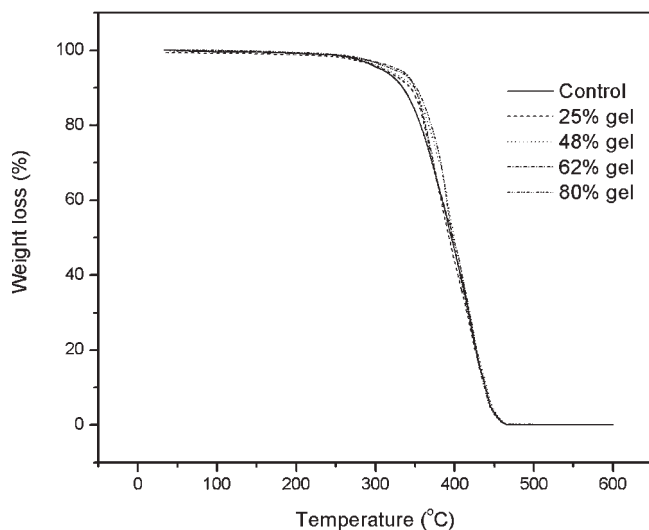


Figure 6 Effect of crosslinking on the thermal stability of PCL.

against the formation of gaseous products on heating.²⁶ This is probably responsible for an increase in the thermal stability of crosslinked PCL. Similar results were also reported for the crosslinking of poly(butylenes adipate-*co*-succinate) by Kim et al.²⁷

Mechanical properties

PCL is ductile; under tension at room temperature, it usually yields with necking and drawing followed by strain hardening and finally ruptures at a relatively long elongation. The data for the effects of the temperature and gel fraction on the tensile properties of control and crosslinked PCLs are summarized in Table II.

At any specified temperature, the elongation at break generally decreases with an increasing gel fraction. Crosslinked samples with 25% gel at 70°C do not rupture in the measurement range. At room temperature, both physical crosslinks and chemical crosslinks exist between polymeric chains. Chemical crosslinks are much stronger than physical cross-

links. With an increase in the chemical crosslinks, the restriction imposed on the elongation behavior of the polymer increases. This restriction is due to the smaller length of the chains available for stretching. Under tensile conditions, the shorter chains reach their maximum extension first and carry a disproportionate part of the load. The greater the crosslinking density is, the shorter the chain is between such links, and the smaller its possible extension is. Hence, a decrease in the elongation at break can be observed with an increase in the gel content. At 70°C, the physical crosslinks disappear as a result of the disappearance of the crystallites. At a low gel fraction, the chemical crosslinks are not yet sufficient to hold the structure fully. Therefore, the sample does not rupture in the measurement range. However, with an increase in the chemical crosslinks, the chemical crosslinks are more effective, although the physical crosslinks disappear. This reduces the elongation at break at high temperatures.

The values in Table II show that the radiation crosslinking of PCL in the presence of TAIC does not have any significant influence on the Young's modulus and stress at yield at room temperature. The Young's modulus and stress at yield at room temperature for a polymer depend more on its crystalline phase than its amorphous content. The crystalline structure is not affected by the introduction of crosslinks into the PCL chain (as shown in Table I), as are the Young's modulus and yield strength. However, with an increase in the temperature, the yield point of the crosslinked samples disappears as a result of melting in the crystalline phase, and a rubberlike behavior can be observed.

Crosslinking has a pronounced effect on the tensile strength. At room temperature, with a low crosslinking level, the tensile strength can be greatly improved. However, the tensile strength decreases with an increase in the gel fraction. This behavior is the result of a loss of drawability because the tensile stress at break is strongly affected by the drawability of the polymer before failure.²⁸ Samples that undergo strain hardening during stretching have a higher

TABLE II
Effects of the Temperature and Gel Content on the Tensile Properties of Control and Crosslinked PCLs

Gel fraction (%)	Elongation at break (%)		Tensile strength at break (MPa)		Modulus (MPa)		Stress at yield (MPa)	
	25°C	70°C	25°C	70°C	25°C	70°C	25°C	70°C
0	1100	—	27.1	—	204	—	14.1	—
25	1010	— ^a	32.5	— ^a	200	3.1	14.7	— ^b
48	895	700	30.3	2.8	209	1.9	14.3	— ^b
62	760	535	25.8	2.1	203	1.3	14.8	— ^b
80	550	396	22.6	1.9	200	1.0	14.5	— ^b

^a The samples did not rupture in the range of the tensile machine.

^b The yield point was not observed.

strength at break than samples that do not undergo strain hardening. With a high gel fraction, the strain hardening of PCL is weakened greatly because of less drawability. Hence a drop in the tensile strength is observed. At 70°C, because of the disappearance of the crystallites, the tensile strength decreases to a great degree compared with that at room temperature.

CONCLUSIONS

The influence of γ radiation on the thermal and mechanical properties of PCL/TAIC has been investigated in this article. DSC analyses have shown principal differences between the first and second scans. From the first scan, we conclude that crosslinking does not have a significant influence on T_m and X_c of PCL. The second scan, however, shows a decrease in T_m and X_c . DMA has shown an increase in T_g as a result of radiation crosslinking. TGA has shown that γ -radiation crosslinking slightly improves the thermal stability of PCL. However, a correlation between the thermal stability and crosslinking level has not been observed.

Moreover, γ radiation strongly influences the mechanical properties of PCL. At room temperature, the tensile strength and elongation at break decrease with an increase in the crosslinking level. However, the Young's modulus and stress at yield are not affected by radiation crosslinking. With an increase in the temperature above T_m , the stress at break, elongation at break, and Young's modulus are also reduced with an increase in the crosslinking level. The yield stress disappears as result of the disappearance of the crystallites.

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