

Pressure-Induced Polymerization of Tetraethylene Glycol Dimethacrylate

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ABSTRACT: The polymerization and crosslinking of tetraethylene glycol dimethacrylate were induced by high pressure. The product was analyzed by both swelling experiments and broadband dielectric spectroscopy to determine the structure, with IR measurements used to follow the extent of reaction and its temperature dependence. © 2008 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 46: 3795–3801, 2008

Keywords: acrylates; crosslinking; degree of polymerization (DP); dielectric properties; molecular dynamics; polymerization; pressure; swelling

INTRODUCTION

Conventional polymerizations usually rely on thermal activation aided by a catalyst; the latter can influence both the chemical and the chain structure (molecular weight and its distribution, branching, etc). Ambient temperature polymerization can be brought about by ionizing radiation, which may be catalyzed or enhanced by sensitizers,^{1–3} and also by hydrostatic pressure. High-pressure synthesis of polymers is important industrially, because the omission of catalysts allows materials of the highest purity to be obtained. However, only a few pressure-induced polymerizations have been reported, for example, polyisoprene,⁴ polyethylene,^{3,5} polypropylene,⁶ paracyanogen,⁷ polyacetylene,⁸ polybutadiene,^{2,9} styrene,¹⁰ and phenylacetylene.¹¹ Often the reactants in these syntheses are unstable even at ambient conditions. Herein, we

describe the pressure-induced polymerization of tetraethylene glycol dimethacrylate (TEGDMA). TEGDMA is used in the manufacture of polyacrylates (“acrylics”), an important technological material used in a broad range of applications (pressure-sensitive adhesives, Superglue[®], Plexiglas[®], resists for electron beam lithography, membranes for filtration and blood dialysis, paints, textile, and optical fibers, etc). There have been many studies of acrylate polymerization,^{12–20} but these methods employ catalysts or, in the case of free-radical polymerization, the use of organic peroxides. There has been no example of the pressure-induced polymerization of acrylates. In this article, we discuss such a process and its advantages over conventional methods of synthesis.

There are different techniques that can be used to monitor changes in the dynamic properties of the reacting species during polymerization. One of them is broadband dielectric spectroscopy that can provide information relating to the viscosity, degree of conversion, and relaxation times of main chain and side-group motions. Polymerization influences the dielectric

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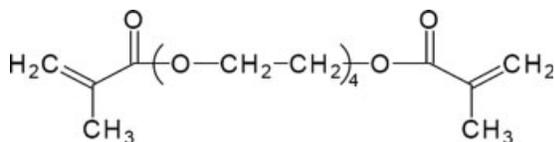
relaxation spectrum through both chemical and physical effects.²¹ Polymerization per se decreases the dc conductivity due to reduced diffusivity of ions and it also increases the local segmental (α -) relaxation time of the main species due to its increasing size and more sterically constrained environment. Fitz and Mijovic²² have analyzed network formation in epoxies from the change of the dielectric strength arising from the reaction of polar groups. They found that while the α -peak is sensitive to network formation, the secondary peaks are not.²³ Viciosa et al.^{20,24} followed the polymerization of *n*-ethylene glycol dimethacrylates from changes in dielectric properties; in particular, the dielectric strength of the main α -relaxation process decreases with the extent of polymerization.

EXPERIMENTAL

TEGDMA (90% pure with 50 ppm hydroquinone as a stabilizer) was purchased from Sigma/Aldrich and used as received. The chemical structure of this compound is presented in Scheme 1. Polymerization and network formation were carried out by application of hydrostatic pressure.²⁵ Briefly, the dielectric cell with liquid sample was placed into a Teflon bellow mounted in the high-pressure chamber. Hydrostatic pressure was generated by displacing the piston by means of a hydraulic press. Pressure was determined from the force exerted on piston (accuracy of 10 MPa). This technique enables pressures of a few gigapascals to be attained. The temperature was controlled within 0.1 K by means of liquid flow from a thermostatic bath.

Swelling experiment involved immersion of a weighed sample in chloroform for 3 days, with daily replacement of the solvent. The swollen gels was patted dry to remove adhered solvent, reweighed, and then dried 24 h in vacuum prior to final weighing. This measurement distinguishes linear and crosslinked polymers, allowing the degree of crosslinking to be determined.

IR measurements were performed using a Bio-Rad FTS-6000 spectrometer equipped with a



Scheme 1. Chemical structure of TEGDMA.

KBr beam splitter, a standard source and a DTGS Peltier-cooled detector. The MIRacle diamond accessory with KRS5 prism was applied to collect spectra in the range 380–4000 cm^{-1} , with a spectral resolution 2 cm^{-1} . The investigations were made at room temperature and usually 32 scans were accumulated. To correct for light sample penetration, the C=O stretching vibration absorption, centered near 1730 cm^{-1} , was used to normalize the data; therefore, all the reported absorbances have been normalized to the integrated area of the C=O vibration.

CALCULATION

Ab initio calculations were performed with the PQS program. The geometry optimization and IR spectra calculation were carried out with density functional theory (DFT)—the B3LYP functional and standard Gaussian polarized and split-valence basis set (6-31G*) were applied. The harmonic vibrational frequencies and IR intensities were recalculated using Pulay's scaled quantum mechanical force field (SQM) methodology.²⁶ This procedure gives good reproduction of the fundamental frequencies and allows assignment of the IR bands. The calculations were done for the TEGDMA molecule, that is, the corresponding dimer (depicted in Fig. 6). To compare the theoretical and experimental results, the theoretical spectra were constructed as a sum Lorentz bands with 5 cm^{-1} full width at half-maximum.

RESULTS AND DISCUSSION

Figure 1 shows the representative dielectric loss spectra of the TEGDMA collected at different times at $T = 303$ K and $p = 1$ GPa. The spectra evolve over time as follows: (i) the α -relaxation and dc conductivity move toward lower frequencies; (ii) the dielectric strength of the main relaxation process decreases; and (iii) the shape of the α -relaxation peak systematically broadens. These changes indicate that the material is polymerizing under these conditions. Experiments performed at the same temperature but lower pressure ($p = 500$ MPa) show polymerization but at a significantly reduced rate. No reaction was observed at ambient pressure ($p = 0.1$ MPa), even at $T = 393$ K. Thus, substantial

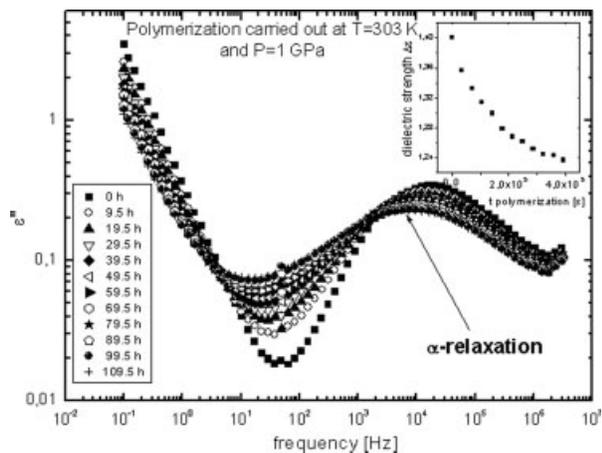


Figure 1. Representative loss spectra obtained during polymerization of TEGDMA performed at $T = 303$ K, $p = 1$ GPa. In the inset, the dependence dielectric strength of the α -relaxation $\Delta\epsilon$ versus time of the polymerization is depicted.

pressure is required to polymerize TEGDMA over feasible time scales.

Figure 1 shows that the α -peak shifts only slightly, about one decade, toward lower frequencies. Generally, this shift during network formation is much more pronounced.^{23,27,28} The gelation of the TEGDMA occurs at low conversion of the monomer, which drastically decreases diffusion of the reacting species, inhibiting the reaction.²⁹ As seen in Figure 1, there is a systematic broadening of the α -relaxation peak, reflecting an increase in the distribution of relaxation times. This is accompanied by a systematic reduction in the strength of the primary α -relaxation (see inset to Fig. 1). The changes in the dielectric strength of the α -relaxation become smaller with time of reaction, indicating that the polymerization is ceasing. Previously it was shown that during crosslinking polymerization of the *n*-ethylene glycol dimethacrylates (DEGDMA, TrEGDMA, TEGDMA), the dielectric strength of the main relaxation process goes to zero with the extent of crosslinking. In partially polymerized samples, the dielectric strength of the α -relaxation process was much weaker than that of the monomer and could vanish with full polymerization.^{20,29} To further characterize the reaction products, dielectric measurements and swelling experiments were carried out.

Figure 2 shows the dielectric loss spectra obtained for the monomer TEGDMA at ambient pressure (Panel a), the polymer obtained at

$T = 303$ K, $p = 1$ GPa, and $t = 96$ h (Panel b) and at $T = 373$ K, $p = 1$ GPa, and $t = 15$ h (Panel c). From data in Panels a and b, glass transitions temperatures were estimated, respectively, as $T_g = 189$ K and $T = 190$ K (T_g defined as the temperature at which $t_a = 100$ s). For the dielectric spectra in Figure 2 (Panel c), no distinct α -peak is evident. Highly crosslinked materials have suppressed T_g (since the crosslinked segments do not undergo a transition to the liquid). The transition is also broadened since the mobility of a segment will depend on its distance from the crosslink junction. For these reasons, very highly crosslinked materials may not exhibit a glass transition. Nevertheless, the putative T_g is expected to be much higher than for the monomer. This increase of T_g with polymerization and crosslinking serves to decelerate and can eventually terminate the chemical reaction. A similar scenario was reported in ref. 30.

Additionally from Figure 2, one can see that the shape of the α -relaxation of the polymer obtained at $T = 303$ K is much broader than that of the monomer. In the spectra for the polymer produced at $T = 373$ K and $p = 1$ GPa, two secondary relaxations appear in the high-frequency range. In earlier work on the catalyzed polymerization of *n*-ethylene glycol dimethacrylate at ambient pressure,^{20,24} two secondary modes were observed in polymerized samples. The slower one (β) was assigned to the hindered rotations of the carboxylic group, whereas the faster one was related to twisting motions within the ethylene glycol moiety.²⁴ Additionally, it was shown that no secondary relaxation changes the frequency with polymerization time. However, the dielectric strength of the β -relaxation decreased with increasing degree of conversion of the monomer, while the γ -relaxation was unchanged. Loss spectra presented in Figure 2 (Panel c) reveal that the position of the γ -relaxation is the same as in monomer, consistent with the general observations of others.^{20,23,31} Note that material produced at $T = 373$ K at $p = 1$ GPa is a hard, transparent solid.

Results from the swelling experiments (Fig. 3) show clearly that polymerization of TEGDMA is accompanied by substantial crosslinking. A plateau is reached at $\sim 12\%$ conversion, with an increasing crosslink density reflected in the reduced degree of swelling. There is a significant increase in the extent of reaction with increasing temperature, as expected.

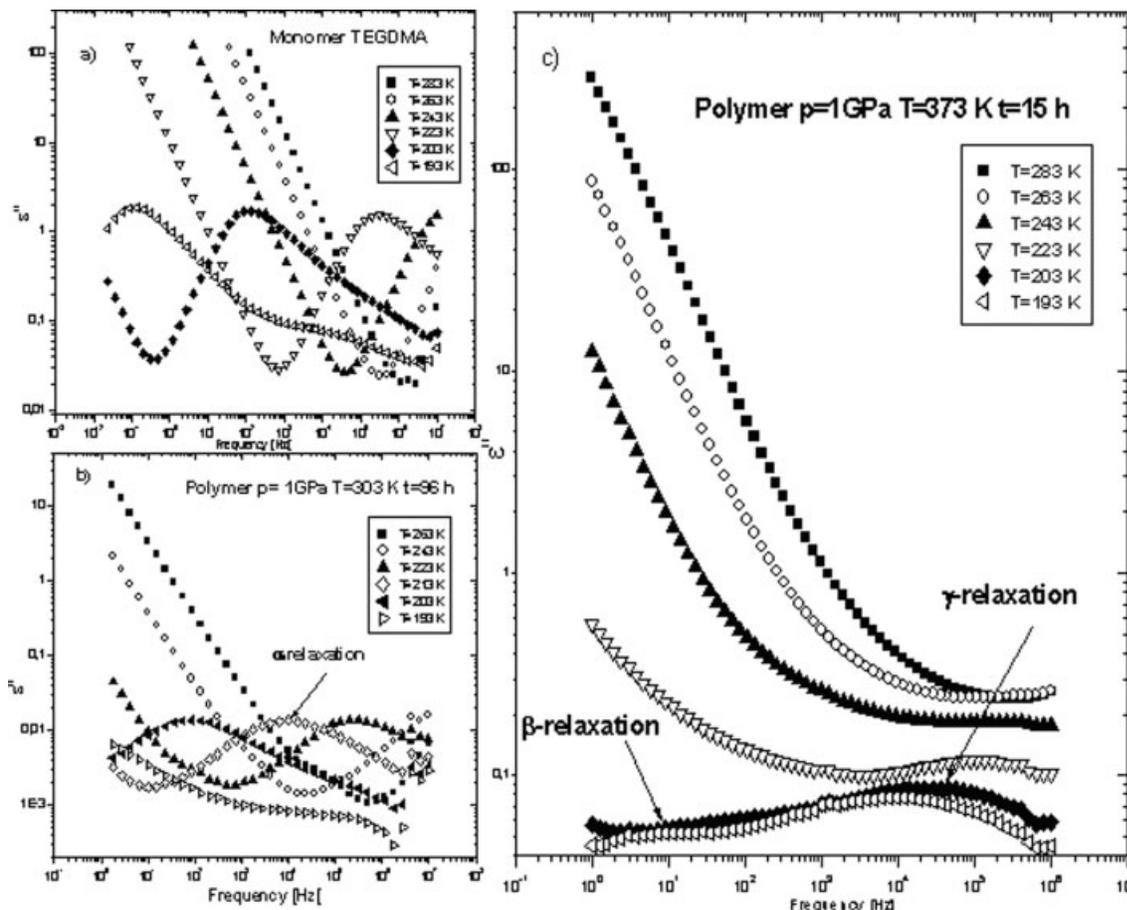


Figure 2. Dielectric loss spectra measured for monomer (Panel a), polymer obtained at $T = 303$ K, $p = 1$ GPa, and $t = 96$ h, (Panel b) and at $T = 373$ K, $p = 1$ GPa, and $t = 15$ h (Panel c) at different temperatures at ambient pressure.

Although the swelling and dielectric spectroscopy results show that TEGDMA undergoes a crosslinking type of polymerization, none of the technique reveals which moieties are responsible for this reaction. For this, we use IR measurements. Figure 4 shows the experimental IR spectra of the monomer and three polymers. The spectrum of the polymer produced at $T = 303$ K at $p = 1$ GPa reveal small differences to that measured for the monomer, while in the spectra for the polymers synthesized at higher temperature these changes become more evident and visible. The main differences between the spectra are for the strong absorption at ~ 1730 cm^{-1} , which is assigned to the stretching C=O vibration, and the band centered around 1650 cm^{-1} , arising from the C=C stretching vibration. The C=O band is sharp and symmetrical in the monomer spectra, and becomes broader and asymmetrical in the polymers. The C=C band

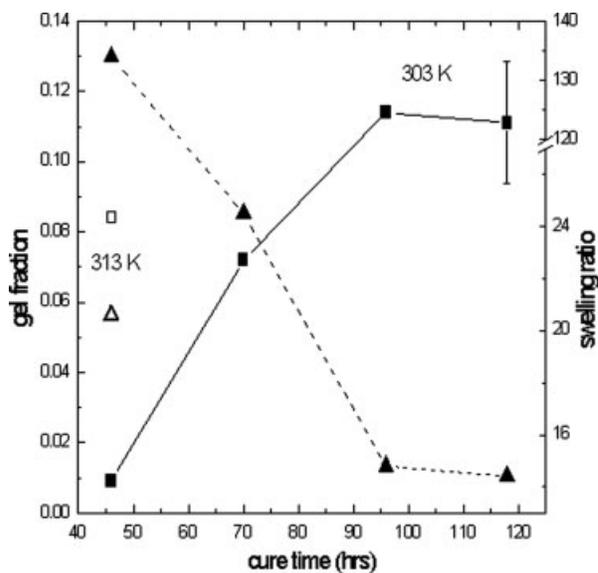


Figure 3. Gel fraction (squares) and swelling ratio (triangles) as function of time at 303 K (solid symbols). The hollow points are data for reaction at 313 K.

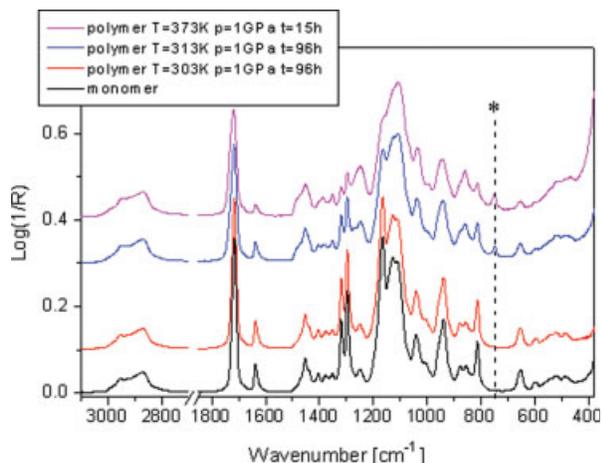


Figure 4. Comparison of the experimental IR spectra of the monomer and polymers obtained at different T at $p = 1$ GPa.

intensity decreases visibly with polymerization, indicating that the reaction of the unsaturated carbons is central to the polymerization reaction. These changes are illustrated more clearly in Figure 5, showing the IR spectra for the monomer and polymer obtained at $T = 373$ K and $p = 1$ GPa in an expanded scale emphasizing the range of frequencies between 1800 and 1600 cm^{-1} . Also in Figure 4 at ~ 750 cm^{-1} (denoted by a dashed line), a new peak appears, whose intensity increases with increasing degree of polymerization.

To better understand these changes, we compare the calculated spectra of the monomer and a dimer of two TEGDMA molecules in Figure 6.

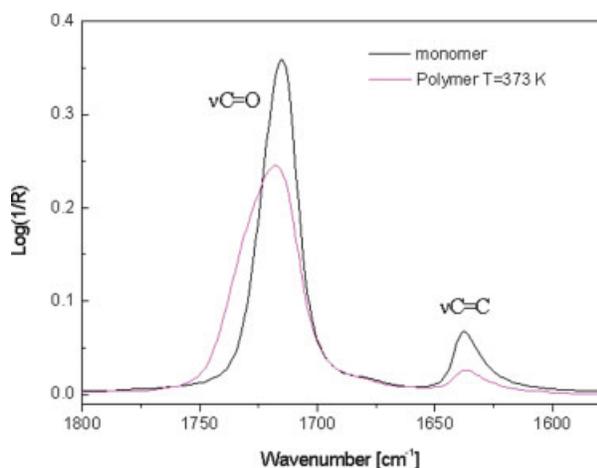


Figure 5. Comparison of the experimental IR spectra of the monomer and polymer obtained at $T = 373$ K and $p = 1$ GPa in the frequency range $\nu = 1600$ – 1800 cm^{-1} .

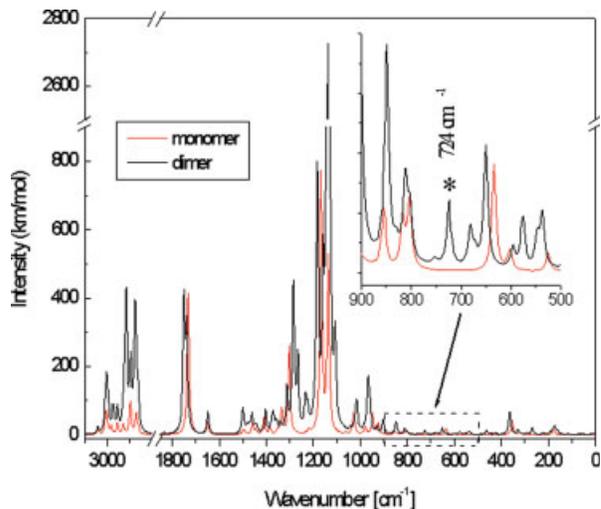


Figure 6. Calculated IR monomer and dimer spectra. The insertion shows low frequency range with the $\delta_r\text{CH}_2$ vibration.

The calculated spectra for the monomer reproduce well the positions and intensities of the experimental spectrum of TEGDMA. We have found that the asymmetry of C=O band in the polymer arise from the different frequency vibration of the C=O group at the end and middle of the molecule; the calculated frequencies are 1740 and 1751 cm^{-1} , respectively. Fitting the experimental spectra yields 1715 and 1728 cm^{-1} . Increasing the degree of polymerization results in an increase of the C=O band height. From the calculated spectra, we also determine that the intensity of the 750 cm^{-1} band in the polymers is due to the rocking motion of the CH_2 groups.

Figure 7 shows the calculated spectra for the dimer and experimental spectra for the polymer

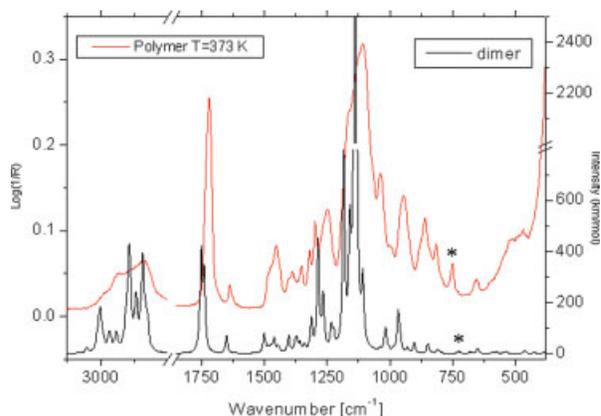


Figure 7. Comparison between the experimental IR spectra of polymer and calculated IR spectra of dimer.

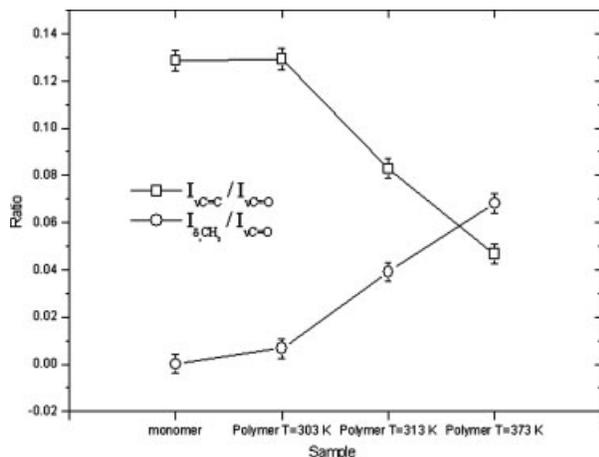


Figure 8. The changes in intensity of the band $\delta_r CH_2$ ($\sim 750\text{ cm}^{-1}$) (circles) and $\nu C=C$ ($\sim 1650\text{ cm}^{-1}$) (squares) versus temperature at which the polymerization reaction was performed. Intensity of the considered bands were calculated in comparison to the intensity of the $\nu C=O$ ($\sim 1730\text{ cm}^{-1}$) band for all polymer samples.

obtained at $T = 373\text{ K}$, $p = 1\text{ GPa}$, and $t = 15\text{ h}$. One can observe that, significant differences are apparent between the spectra. These discrepancies are caused by the structure of the network polymer, which is more complicated than the simple dimer, on which the calculation was based.

Figure 8 shows the intensity of the band at $\sim 750\text{ cm}^{-1}$ (motion of the CH_2) and at $\sim 1650\text{ cm}^{-1}$ ($C=C$ motion) as a function of polymerization temperature. The changes in intensity of these considered bands were compared with the intensity of the $C=O$ band at $\sim 1730\text{ cm}^{-1}$. The latter group is not active during the polymerization of the TEGDMA, and in fact despite some broadening, its integral intensity is invariant. From Figure 8 it is seen that with increasing temperature of polymerization, there is a pronounced decrease in intensity of the $C=C$ band and an increase in the CH_2 band intensity. Thus, these absorptions can be used as indicators of the polymerization. The highest degree of conversion of double bonds was achieved at $T = 373\text{ K}$ and at $p = 1\text{ GPa}$. From the integral intensities of the $C=C$ bands for the monomer and polymer reacted at $T = 373\text{ K}$ and $p = 1\text{ GPa}$, the degree of conversion of double bonds was determined to be 65%. This is less than full reaction; however, complete (100%) conversion is not attainable.

CONCLUSIONS

In this article, we describe the high-pressure polymerization of TEGDMA. A pressure of 1 GPa was required to observe reaction over laboratory timescales. The conversion of the monomer, as revealed by dielectric and IR measurements, was reached at the highest temperature, 373 K, at this pressure.

Although this is a very high pressure, it is low in comparison to pressures used previously to induce polymerization. The degree of cross-linking (12%) of the polymer produced near room temperature ($T = 303\text{ K}$ at $p = 1\text{ GPa}$) compares favorably to results for the industrial-scale production of PMMA ($c = 7\text{--}10\%$). The highest level of conversion achieved (at $T = 373\text{ K}$ and $p = 1\text{ GPa}$) was about 65%, based on the loss of unsaturation. An advantage of pressure-induced polymerization is the potential for exceptional purity of the products (determined by the purity of the monomer) given the absence of catalysts and solvents as well as environmental advantages of avoiding catalysts and high reaction temperatures. Finally, while catalyzed polymerization of TEGDMA at ambient pressure has only been above $T = 343\text{ K}$, at $p = 1\text{ GPa}$ polymerization initiated at 303 K.

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