Crosslinking polymerization of tetraethylene glycol dimethacrylate under high pressure.

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Abstract: The polymerization reaction of tetraethylene glycol dimethacrylate was induced by application of high pressure. Broadband dielectric spectroscopy was employed to investigate dielectric properties of the produced polymers. Additionally swelling experiment was performed to determine the degree of crosslinking of the polymers.

Key words: Polymerization, high pressure, acrylates

1. Introduction

The utility of polymers can scarcely be overstated, whether as simple commodities or in technically advanced optical and electronic applications. The conventional method of polymerization is thermally, usually with a catalyst; the latter can influence both the chemical structure and the macrostructure (molecular weight and its distribution, branching, etc.). Ambient temperature polymerization can be brought about by ionizing radiation, often catalyzed or enhanced by sensitizers [1,2,3], and also by hydrostatic pressure. High pressure syntheses of polymers are very important from an industrial point of view, because the omission of catalysts can yield materials of the highest purity. Reports of pressure-induced polymerization are limited to a few examples, polyisoprene [4], polyethylene [3,5], polypropylene [6], paracyanogen [7],
polyacetylene [8], and polybutadiene [2,9], with the reactants in these polymerizations often unstable even at ambient conditions. Here we present pressure induced polymerization of tetraethylene glycol dimethacrylate (TEGDMA). This compound is used in the manufacture of polyacrylates (“acrylics”), important technological materials for a broad range of applications (pressure-sensitive adhesives, Superglue®, Plexiglass®, 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 [10,11,12,13,14,15,16,17,18], but these methods rely on catalysts or, in the case of free radical polymerization, the use of a peroxide. There has been no example of the pressure-induced polymerization of acrylates. In this paper we describe a new polyacrylate synthesis having advantages over conventional methods.

Pressure-induced polymerization influences the dielectric relaxation spectrum through both chemical and physical effects [19]: Polymerization per se decreases the dc conductivity due to reduced diffusivity of ions and increases the local segmental (α-) relaxation time of the main species due to its increasing size and more constrained nature. There are concomitant physical effects due to the direct dependence of molecular mobility on hydrostatic pressure. Fitz and Mijovic [20] 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 [21]. Viciosa et al. [18] followed the polymerization of triethylene glycol dimethacrylate from changes in dielectric properties; in particular the dielectric strength of the main α-relaxation process decreases with the extent of polymerization.
2. Experimental

TEGDMA (90% pure with 50 ppm hydroquinone as a stabilizer) was purchased from Sigma/Aldrich and used as received. Scheme of the tetra ethylene glycol dimethacrylate is presented below

![Scheme 1](image)

**Scheme 1** The chemical structure of tetraethylene glycol dimethacrylate

Polymerization and network formation were carried out by application of hydrostatic pressure. Briefly the dielectric cell with liquid sample was placed into a teflon bellows 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 experiments involved immersion of a weighed sample in chloroform for three days, with daily replacement of the solvent. The swollen gels was patted dry to remove adhered solvent, reweighed, and then dried 24 hrs in vacuo prior to final weighing.

3. Result and discussion

During dielectric measurements carried out at $T=303$ K and $P=1$ GPa one can observe characteristic changes in the dielectric loss spectra (decrease in dc conductivity, slightly decrease
in dielectric strength of main \( \alpha \)-relaxation peak) consistent with polymerization. Simultaneously, the TEGMDA changed its consistency from a normal liquid to a gel (see Fig. 1)

![Photography showing the polymerized tetraethylene glycol dimethacrylate](image)

**Figure 1** Photography showing the polymerized tetraethylene glycol dimethacrylate

Experiments at the same temperature but lower pressure (500 MPa) indicated some polymerization at a much reduced rate, while no reaction was induced at ambient pressure (0.1 MPa). Evidently polymerization of the TEGMDA is initiated only by sufficiently high pressure; that is, there appears to be a threshold value in order to achieve a measurable reaction rate.

Since we know that TEGDMA polymerizes under high pressure, swelling experiments and dielectric measurements were carried out to see which type of polymer is produced: crosslinked or linear.
Swelling experiments were performed on the samples obtained at T=303 K and P=1 GPa after different reaction times. The fact that not all the material is soluble shows clearly that polymerization of TEGMDA is accompanied by substantial crosslinking with consequent gel formation.

![Swelling ratio and gel fraction vs. cure time](image)

**Figure 2** 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.

This network formation is seen in the swelling data in Fig. 2. A plateau is reached at ~ 12% conversion, with an increasing crosslink density reflected in the reduced degree of swelling (due to the competition between maximizing the mixing entropy and minimizing the elastic strain energy). Also included in Fig. 2 (open symbols) are the data measured for reaction at P=1 GPa and T=313 K for 46 hours). These data are presented to show that there is a substantial increase in the extent of reaction with increasing the temperature. Therefore by performing the
polymerization of the TEGDMA at higher temperature we showed that it is possible to reduce the time of the polymerization to reach nearly the same degree of conversion ($c \approx 9\%$) as in the case of polymer obtained at $T= 303 \text{ K} \ p= 1 \text{ GPa}$ and $t= 96 \text{ h}$ ($c \approx 12\%$). For comparison on an industrial scale $c$ for polymethyl methacrylate (PMMA) is within the range of 7 to 10%.

Fig. 3 displays spectra obtained for the monomer TEGDMA at ambient pressure (a), the polymer obtained at $T=373 \text{ K}, \ p=1 \text{ GPa}, \ t=15 \text{ h}$ (b) at $T=303 \text{ K}, \ p=1 \text{ GPa}, \ t=96 \text{ h}$ (c) Additionally we depicted the superposed dielectric loss spectra of the monomer with that of the polymer obtained at $T=303 \text{ K}, \ p=1\text{ GPa}$ after $t=96 \text{ h}$ (d), the latter shifted along the frequency axis to coincide with the monomer data at 207 K. (Note that the dc conductivity contribution were subtracted from both spectra.)
Figure 3 Dielectric loss spectra measured for monomer (a), polymer obtained at $p=1\text{GPa}$, $T=373 \text{ K}$, $t=15 \text{ h}$ (b), $T=303 \text{ K}$, $p=1\text{GPa}$ and $t=96 \text{ h}$ (c). At panel (d) the superposed dielectric loss spectra of the monomer (filled squares) and polymer obtained at $T=303 \text{ K}$ $p=1\text{GPa}$ after $t=96 \text{ h}$ (open circles) are presented. Both spectra were measured at $T=207 \text{ K}$.

One can see that the shape of the $\alpha$-relaxation of the polymer obtained at $T=303 \text{ K}$ is much broader than that of the monomer see panel (d). Reduction in the slope on the low frequency side of $\alpha$-peak is also clearly visible. Thus these two effects, broadening of $\alpha$-peak and change in steepness on the low frequency side of the structural relaxation of the polymer, are next evidences about crosslinking type of polymerization of the TEGDMA. It should be noted that similar scenario was observed during network polymerization induced by AIBN initiator in the triethylene glycol dimethacrylate [18] and in the case of crosslinking polymerization of the epoxy amine systems [22,23]. Additionally in panel (b) it is shown there is no $\alpha$-relaxation peak in the wide range of temperatures for the polymerization product at $T=373 \text{ K}$. It is commonly observed that during crosslinking polymerization the dielectric strength of the main process goes to 0 ($\Delta\varepsilon\to0$) with increasing degree of crosslinking [18,22,23], since the $\alpha$-dynamics are suppressed; this accounts for the absence of the peak after reaction at $T=373 \text{ K}$, $p=1\text{GPa}$ and $t=15 \text{ h}$. Furthermore lack of the structural relaxation peak in dielectric loss spectra of the polymer obtained at $T=373 \text{ K}$ at $p=1\text{GPa}$ is an evidence about large molecular weight and significant crosslinking of the polymer produced at this condition. In the dielectric spectra collected for polymers produced at $T=373 \text{ K}$, $T=303 \text{ K}$ and $p=1\text{GPa}$, a secondary relaxation appears in the high frequency range. The position of this $\beta$-relaxation is the same as for the monomer. It is consistent with the observation made by Mijovic and Viciosa [18,20, ] that secondary relaxations are insensitive to crosslinking.
The characteristic changes in the loss spectra during the reaction (data for 303 K and 1 GPa shown in Fig. 4) reveal the chemical moieties that are likely responsible for the polymerization. The small decrease in the dielectric strength of $\alpha$-peak with time suggests the reaction involves the unsaturated carbons, which make only a small contribution to the total dipole moment of TEGDMA. This conclusion is unsurprising, since in all cases of pressure induced polymerization, the double bonds between carbon atoms are the active centers for polymerization. Note that reaction of the ester moiety would cause a much greater reduction in the dielectric strength.

![Polymerization carried out at T=303 K and P=1 GPa](image)

**Figure 4** Representative spectra obtained during polymerization of TEGDMA performed at T=303 K, p=1 GPa. In the inset dependence of the dielectric strength of the $\alpha$-relaxation vs time of polymerization is shown
Fig. 4 also indicates that during polymerization of the TEGDMA, the $\alpha$-peak shifts only slightly towards lower frequency. Generally, this shift during network formation is much more pronounced [21,24,25]. The behavior is a result of gelation of the TEGDMA during polymerization. Unfortunately this process occurs at low conversion of the monomer and leads to a drastic decrease in diffusion coefficient of the reacting species, ultimately inhibiting the polymerization reaction; thus, reaction occasions little change in the position of the primary $\alpha$-peak. As shown in Fig. 1, there is systematic broadening of the $\alpha$- relaxation peak with time of polymerization, along with a decrease in dielectric strength of the primary $\alpha$-relaxation (see inset to the Fig. 1). Both effects were discussed earlier in this paper.

4. Conclusion

In this paper we demonstrated that TEGDMA undergoes a crosslinking type of polymerization, the first time this has been reported in the literature. Moreover, the threshold value of pressure, $P=1$GPa, needed to initiate polymerization is one of the lowest reported for high pressure induced polymerization.

The formation of a network, together with the increasing chain length, suppresses the mobility of the reacting species. However, this can be circumvented to some extent by increasing the temperature as was shown for polymer obtained at $T=373$ K. To maintain a constant rate of reaction would require a concomitant increase in pressure. The optimum conditions can be deduced from consideration of the relevant activation energies and activation volumes.

Finally it should be noted that the degree of conversion of TEGDMA $c=12\%$ is very satisfactory, in comparison to the values achieved for compounds polymerized on an industrial scale, such as ethylene $c\approx10\%$ propylene $c\approx10\%$ or methacrylate methyl $c\approx5-7\%$. We expect this
method of synthesis of acrylates can be a useful alternative route for producing these type of materials.

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