The preparation of new polymers by the high pressure polymerization of trivinyl benzene

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1,3,5-Trivinyl benzene has been thermally polymerized at temperatures of 150°–340°C and pressures of 0.37–1.0 GNm^{-2}. The results show that the extent of conversion of the vinyl groups present, the density and modulus of rigidity of the polymer all increase with the temperature and pressure of polymerization. The highest moduli are more than three times those of polystyrene.

Specific heats also fall as the density is increased. None of the crosslinked materials show a change in specific heat of the type associated with a glass transition at temperatures up to 500K.

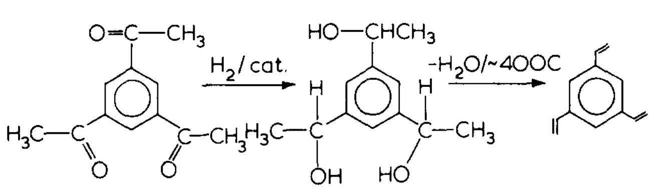
INTRODUCTION

In a previous paper the effect of pressure on the polymerization of *p*-divinyl benzene was described[1]. It was found that when this monomer was reacted at high pressures the polymers obtained had a greatly increased density accompanied by much higher elastic moduli. These results raise a number of interesting points. For example the relatively low modulus of most isotropic polymer glasses is often a disadvantage so that the development of stiffer material would be potentially useful. That this is inherently possible for organic materials is demonstrated by the high moduli of diamond and also of carbon fibres and certain highly oriented polyethylenes[2]. There is also a further, and more fundamental point which raises the question of the structure of a highly crosslinked polymer. It may be supposed that a closely crosslinked covalent network should have a particular geometric structure in space, which cannot change without the fracture of covalent bonds. The conformation, and more particularly the volume of such a structure may reflect the conditions under which it was made as well as its chemical composition. Thus such a crosslinked polymer does not have a characteristic density, as is the case with most materials where atoms and polymer segments can move to equilibrium positions in relation to each other. This somewhat novel expectation was generally confirmed in the previous work[1].

In view of the interest raised by the above points we felt that a confirmation and if possible an extension of the previous results would be desirable. Particularly it was felt that the study of monomers having a high concentration of reactive vinyl groups would be desirable. We have therefore studied the polymerization of trivinyl benzene under a range of pressures up to 1.0 GNm^{-2} and in this paper we report on the properties of the polymers so obtained.

EXPERIMENTAL

1,3,5-Trivinyl benzene was made using the method of Mowry and Ringwald[3] shown below



However, in following their procedure some difficulties were encountered with the dehydration step, and we eventually carried this out by vacuum distillation of the pure triol through the pyrolysis tube over Linde 3A molecular sieves at 370°C. The purity of the final product was checked by g.p.c., i.r. and ^1H n.m.r. spectroscopy.

Polymerization

Here the most important problem was that of encapsulating the polymer in the pressure chamber. For reasons of cost it was not possible to use the gold envelope previously employed[1] and Teflon tubing proved difficult to seal. These difficulties were overcome by using 5 mm o.d. thin walled silver tubing which we were able to close tightly at each end and so to obtain generally bubble free products. These capsules were placed in an argon pressurized apparatus consisting of three interconnected steel chambers, into all of which liquid argon was initially condensed. Each in turn of the first two was then allowed to warm to ambient temperature thus pressurizing the remainder of the system which could then be isolated by suitable valves. The final chamber was provided with a heating jacket, permitting slightly higher pressures and higher temperatures to be employed. Pressures up to 0.70 GNm^{-2} were attainable in this apparatus, the limiting factor arising from the rating of the valves. Using this apparatus, which will be described in more detail else-

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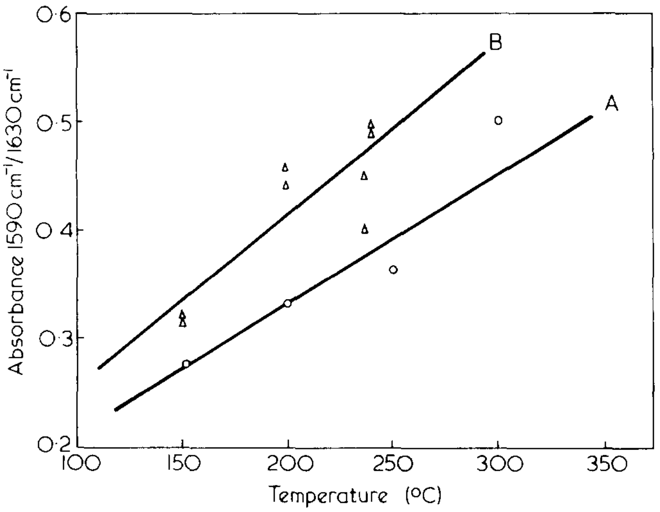

Figure 1 Effect of polymerization temperature on the conversion of pendant vinyl groups for polytrivinyl benzene. The relative conversion is measured by the i.r. absorbance ratio 1590 to 1630 cm^{-1}. A, 0.37 GNm^{-2}; B, 1.0 GNm^{-2}

where[4], a minimum of 2, and more usually 4 ampoules were employed.

As before, thermal polymerization without catalyst was found to be quite satisfactory. This was effected by raising the temperature of the reactor over a period of hours and maintaining the stated temperature for 3 h except with temperatures above 300°C where 1½ h was employed. In line with previous work it was found that the products obtained under the conditions used were not strongly affected by reaction time.

As our pressure equipment was limited to 0.7 GNm^{-2} we arranged for a few further experiments to be carried out at the University of Reading at 1.0 GNm^{-2}. These samples were held at the named temperatures for 2–3 h.

Spectroscopy

Infra-red spectra were run on a Perkin–Elmer instrument, using liquid films, KBr discs (for polymer samples) and mulls as appropriate. ^{1}H n.m.r. spectra were run on a Varian XL-100 instrument at 100 mHz in CCl_4, or $CDCl_3$ solvents, using TMS as internal standard.

Modulus measurements

Modulus measurements were carried out on polished polymer samples at RAPRA, using similar ultrasonic equipment to that previously described[1].

Density measurements

These were performed by titration using mixtures of water and concentrated calcium nitrate solution and checked by a hydrometer at 23°C.

RESULTS AND DISCUSSION

Polymerization by the methods described above leads to highly crosslinked polymers with densities which depend on the conditions of polymerization. It is believed that the mechanical properties of the polymers derived from this process are determined by:

(a) The extent to which double bonds pendant to the initially formed polymer are polymerized. This controls the closeness of the covalent network mesh.

(b) The density of the polymerized product which is determined both by (a) above and by the pressure (density) of the fluid which is being polymerized.

In the previous work we estimated quantitatively the extent of conversion of the second double bond in divinyl benzene. With trivinyl benzene this problem becomes more difficult and we have qualitatively observed the degree of reaction of the pendant double bonds by means of the ratio of the vinyl and aromatic absorbances at 1630 and 1590 cm^{-1}. A selection of these results are plotted in *Figure 1* in which an increase in the observed ratio measures the extent of conversion of pendent double bonds. It will be seen that the ratio increases, as might be expected, with polymerization temperature.

A somewhat similar situation is illustrated in *Table 1* where we show results in which *p*-divinyl benzene and trivinyl benzene were simultaneously polymerized in separate capsules in the pressure chamber. At lower temperatures there is little difference between the densities of the polymers obtained from either of the two monomers, but at 250°C and above, the trivinyl benzene gives a higher density product, as might be expected with a closer meshed network.

The effect of temperature and pressure on the density of the polymers obtained is shown in *Figure 2* where density is plotted against reaction temperature at three different pressure levels. Although there is some scatter in the results the trend to higher density with temperature is clearly shown at each pressure level. This increase in density was shown in the previous paper to be accompanied by an increase in the elastic modulus. These conclusions have now been repeated and confirmed with trivinyl benzene. The results, which are illustrated in *Figure 3*, show a higher slope of the rigidity modulus against density than with divinyl benzene. However, there were indications in the previous paper[1] *Figure 8* that the slope for DVB was on the low side, and when this is taken together with the scatter in the present results we would not wish to claim a significant difference in the modulus density relation between polymerized DVB and TVB. On the other hand the present results directly confirm the trends shown in the previous work, and especially the conclusion that high modulus polymer can be prepared by the high pressure polymerization of polyvinyl compounds. It will be seen that the highest moduli observed in the present work are higher by a factor of 4 compared with the reported rigidity modulus for polystyrene (1.2 GNm^{-2} – ref 5).

Table 1 Comparison of the densities of *p*-divinyl benzene and trivinyl benzene polymerized under different temperatures and pressures

Polymerization		Density	
Temperature (°C)	Pressure (GNm^{-2})	DVB	TVB
150	0.62	1.107	1.105
195	0.64	1.130	1.128
210	0.38	1.108	1.109
250	0.59	1.140	1.149
255	0.38	1.118	1.129
280	0.64	1.153	1.164
305	0.67	1.147	1.165
340	0.67	1.155	1.169

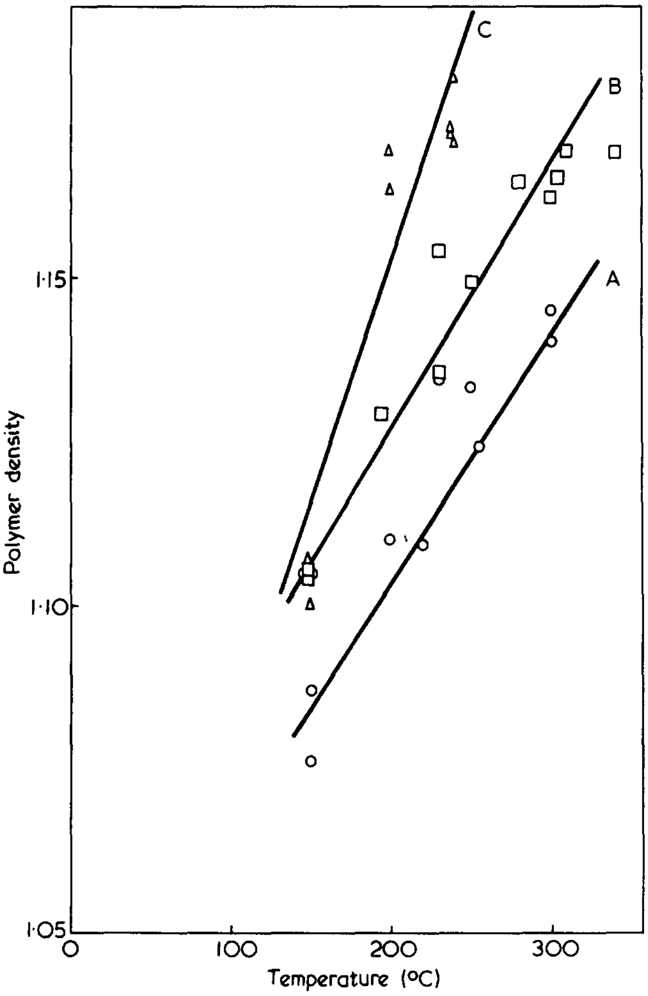

Figure 2 Polymer density plotted against polymerization temperature for trivinyl benzene. Polymerization pressure: A, 0.37 ± 0.02 GNm^{-2}; B, 0.62 ± 0.05 GNm^{-2}; C, 1.00 GNm^{-2}

Specific heat of highly crosslinked polymers

Specific heats were determined by Dr J. N. Hay using a Perkin–Elmer DSC 2 as previously described for polystyrene[6] and the results obtained are presented in *Figure 4*. It will be seen that all the crosslinked poly-trivinyl benzenes have lower specific heats than polystyrene in the glassy state and that this difference increases above the glass transition temperature of the polystyrene. None of the crosslinked materials shows evidence of a glass transition below 500K from which we conclude that the type of motion occurring with polystyrene above T_g has been totally supressed. The specific heat of diamond is included for comparison. It can be seen that, as with the modulus, the specific heat of those highly crosslinked materials is moving in towards the level associated with a diamond structure.

ACKNOWLEDGEMENTS

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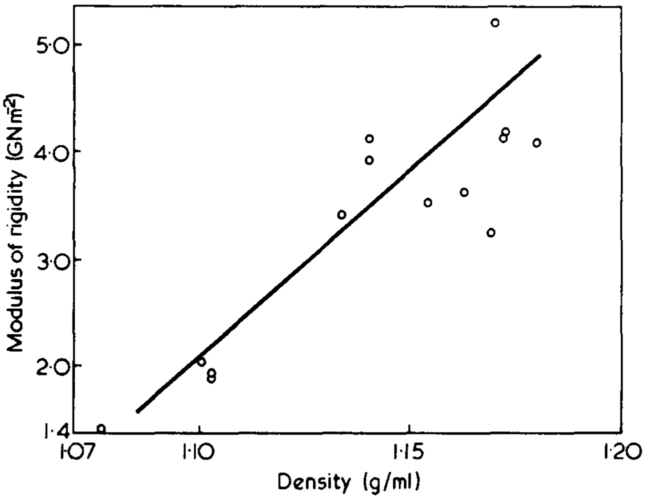

Figure 3 Modulus of rigidity plotted against density for polytrivinyl benzene

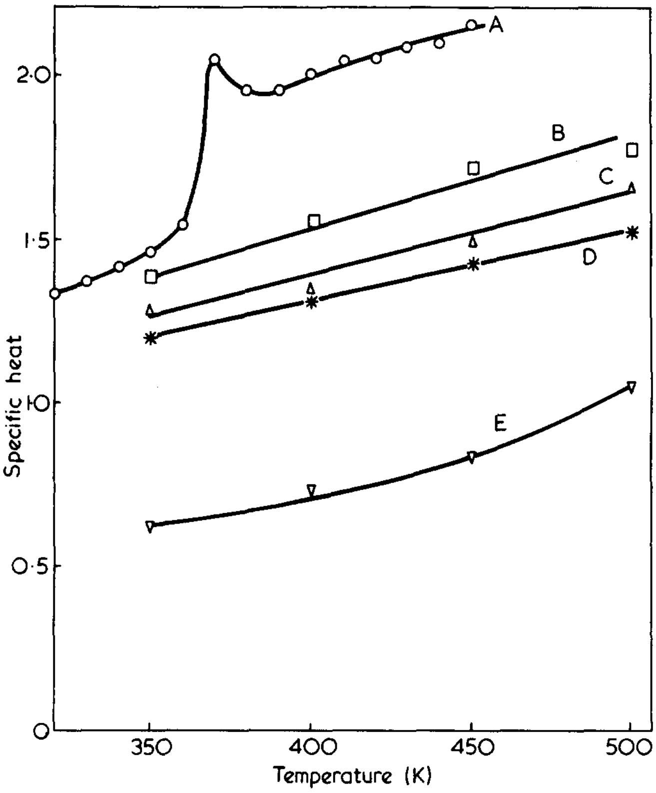

Figure 4 Specific heat plotted against temperature for A, polystyrene, density 1.05, polytrivinyl benzene; B, density 1.087; C, 1.133; D, 1.169; and diamond, E, 3.50. Polystyrene narrow distribution *MW* 19.8 x 10^3

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