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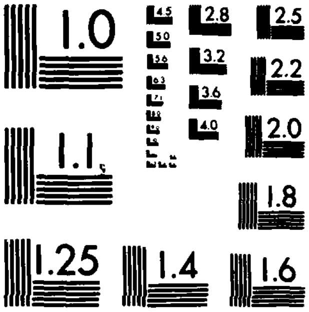

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Synthesis and free-radical curing reactions of the bis-glycidylmethacrylate of bisphenol-A (Bis-GMA) were investigated. Bis-GMA resin was synthesized by reacting Epon 825 with methacrylic acid, followed by characterization using IR and NMR spectroscopy. Various modifiers having reactive double bonds were co-cured with the methacryloxy resins, using a free radical initiator. The networks obtained were compared with a cycloaliphatic amine cured epoxy network. Thermal characterization shows that methacryloxy cured systems are

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more resistant to mechanical penetration and have higher glass transition temperatures and better stability to thermal decomposition as compared with the conventional diamine cured epoxy networks. Dynamic mechanical experiments and stress-strain tests also indicate that Bis-GMA based networks have higher tensile moduli and lower elongation at break. Using different modifiers such as 2-ethyhexyl acrylate, the tensile and impact properties of the networks can be improved.

SYNTHESIS AND CHARACTERIZATION OF FREE RADICAL CURED BIS-METHACRYLOXY BISPHENOL-A EPOXY NETWORKS

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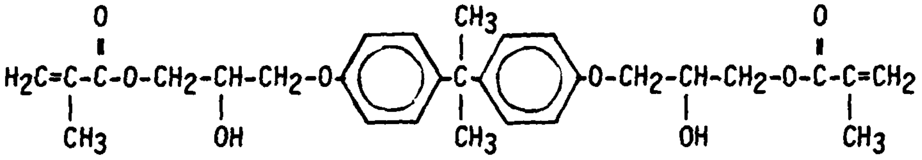
ABSTRACT

Synthesis and free-radical curing reactions of the bis-glycidylmethacrylate of bisphenol-A (Bis-GMA) were investigated. Bis-GMA resin was synthesized by reacting Epon 825 with methacrylic acid, followed by characterization using IR and NMR spectroscopy. Various modifiers having reactive double bonds were co-cured with the methacryloxy resins, using a free radical initiator. The networks obtained were compared with a cycloaliphatic amine cured epoxy network. Thermal characterization shows that methacryloxy cured systems are more resistant to mechanical penetration and have higher glass transition temperatures and better stability to thermal decomposition as compared with the conventional diamine cured epoxy networks. Dynamic mechanical experiments and stress-strain tests also indicate that Bis-GMA based networks have higher tensile moduli and lower elongation at break. Using different modifiers such as 2-ethylhexyl acrylate, the tensile and impact properties of the networks can be improved.

INTRODUCTION

The extreme versatility of epoxy resins have led to their wide-spread application in numerous industrial products. As is very well known, the epoxy networks can be formed by using a large variety of curing agents, including amines, acid anhydrides, Lewis acids, etc. Recently, bis-acryloxy or bis-methacryloxy derivatives of typical epoxy resins [also known as bis-glycidyl(meth)acrylate of bisphenol-A, Bis-GMA], 1, and networks obtained by curing them with free radical polymerization initiators have gained importance and have found applications in many areas, especially as reinforced thermosetting plastics (RTP) and as matrix materials for fiberglass reinforced plastics (FRP) (1,2). They are reported to have convenient and predictable curing reactions with low exotherms and low shrinkage (3). Improved mechanical properties and good resistance to corrosive chemicals at relatively high temperatures compared to other network systems has also been noted (4). Current materials having the structure 1, are usually diluted with styrene and co-cured. However, a wide variety of commerically available vinyl monomers can be used as comonomers or modifiers in these systems and new concepts in the molecular design of networks could yield a spectrum of novel thermosetting resins with diversified properties. The performance of the networks produced will be strongly dependent on the concentration, properties and the reactivity of the modifier(s) used. Under controlled conditions and by proper choice of the modifier, it is also possible to obtain



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characteristic morphologies (e.g. phase separation) for the cured resins (5,6). Very little work has been published in the open literature and hence not much information has been available on the basic characterization of free radically cured Bis-GMA type networks. However, there are many publications which discuss the synthesis and characterization of interpenetrating polymer networks obtained by simultaneously curing Bis-GMA and epoxy resins by using free radical initiators and amine hardeners (6,7).

In this paper, we report some initial investigations of the synthesis and curing reactions of Bis-GMA. Various modifiers with reactive double bonds were used and the products were characterized by thermal analysis IR and NMR spectroscopy. Dynamic mechanical and stress-strain behavior of the networks were also investigated and compared with the cycloaliphatic amine cured epoxy network.

EXPERIMENTAL

Materials:

Epoxy resins Epon 825 and Epon 828 were kindly supplied by the Shell Chemical Company. The epoxy equivalents were 175 and 180 g/equiv. respectively, as obtained by titration (8). Methacrylic acid and styrene were obtained from Aldrich Chemical Co. 2-Ethylhexyl acrylate was a product of Polysciences, Inc. 1,3-Divinyltetramethyldisiloxane was obtained from Silar Laboratories, Inc. and the cycloaliphatic diamine, bis(4-aminocyclohexyl)-methane (PACM-20), was provided by DuPont.

All chemicals were used as received, without further purification.

Synthesis of Bis-GMA and Curing Reactions:

To a three necked 250 ml flask, fitted with a condenser, thermometer and mechanical stirrer, were introduced 102.0 g (0.29 mole) of Epon-825, **2**, and 51.0 g (0.59 mole) methacrylic acid. Then 0.047 g of butylated hydroxy toluene (~0.03 % of total resin weight) was added as free-radical inhibitor. Triphenyl antimony, 1.53 g (~1% by weight) was used as catalyst. The reaction temperature was 95±1°C. The reaction was carried out for 96 hours.

After the esterification was complete as judged by IR spectroscopy, 1.53 g dicumylperoxide and the desired amounts of modifiers were added into the flask, mixed well with the Bis-GMA produced and the mixture was then poured into a preheated RTV-silicone mold. The resin was cured at 160°C for 24 hours.

Network structures derived from Epon-828 and PACM-20 were obtained by mixing stoichiometric amounts of the amine and epoxy resins, degassing at 60°C under vacuum, pouring into a silicone mold and curing at 160°C for 2.5 hours.

Thermal Characterization:

Thermal characterization of the networks were performed by using a

Perkin-Elmer System 2. DSC scans were obtained with a heating rate of 10°C/min, under a N_2-purge. Penetration behavior (TMA) was studied between 70 and 240°C, with a heating rate of 10°C/min and a load of 200 g. Thermal decompositions (TGA) were carried out under nitrogen atmosphere, between room temperature and 600°C, with a heating rate of 20°C/min.

Mechanical Behavior

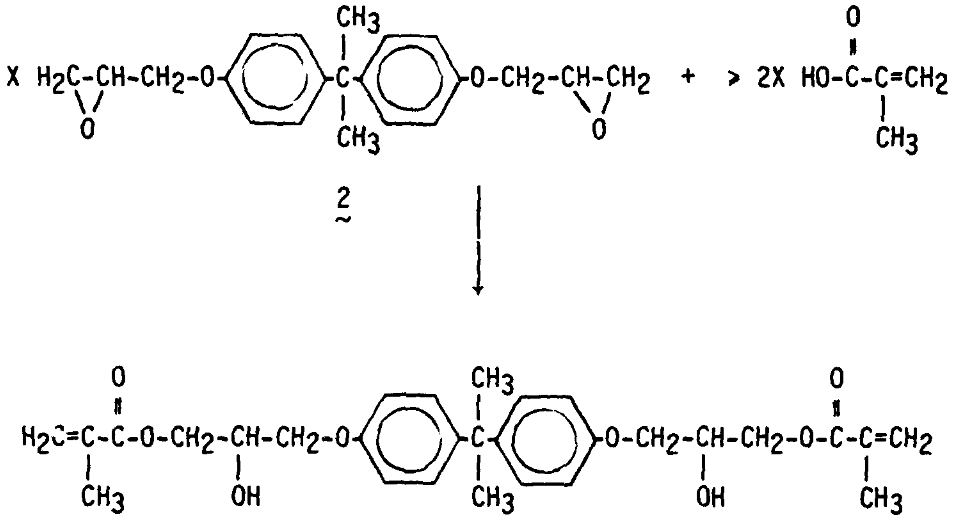
Dynamic mechanical data were obtained between 0 and 260°C, using a Direct Reading Dynamic Viscoelastometer, Rheovibron DDV-IIc of Toyo Baldwin Co. Ltd., Tokyo Japan (IMASS Inc., Accord, MA). Measurements were taken at approximately 3-4°C intervals, except near the relaxation maxima, where the interval was sufficiently small to locate the loss peak accurately. Experiments were carried out under nitrogen, with a heating rate of 1°C/min at a constant frequency of 110 Hz.

The stress-strain data were obtained by using an Instron Model 1122 Tester. Dog-bone shaped samples were tested at room temperature using a crosshead speed of 1.0 mm/min.

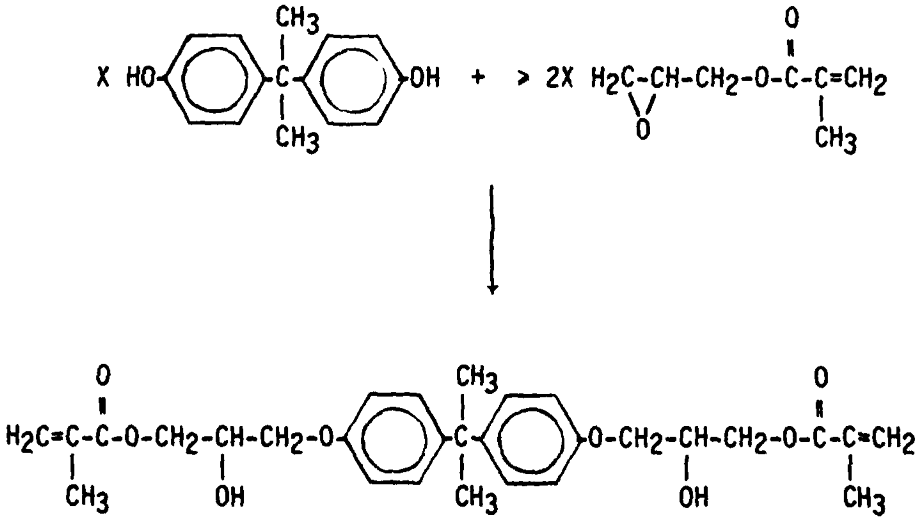
RESULTS AND DISCUSSION

Bisglycidylmethacrylate of Bisphenol-A, Bis-GMA, (or any similar bis-methacryloxy resin) can easily be prepared by the base catalysed reaction of unsaturated acids with the appropriate epoxy resins (Route I), by the base catalyzed reactions of bisphenol-A with glycidyl esters of unsaturated acids (Route II), or by other methods (9,10,18)

Route I



Route II



These reactions can be followed by monitoring the decrease in the carboxylic acid peak at 1705 cm^{-1} and the increase in the ester peaks at ~1730 cm^{-1} and ~1160 cm^{-1} by IR spectroscopy (Route I), or more precisely by titrating the unreacted acid (Route I), or epoxy groups using standard methods (Route I and II).

For the present work, we used triphenyl antimony as the catalyst and followed Route I. Bis-GMA resin produced was characterized by ^1H-NMR and IR spectroscopy. A typical IR spectrum (Figure 1), shows the characteristic absorption bands for hydroxyl groups between 3600-3300 cm^{-1}, a broad ester carbonyl band at 1730 cm^{-1}, an unsaturated C=C absorption at 1640 cm^{-1} and typical bands for a substituted aromatic ring at 1050 and 840 cm^{-1}. Absence of carbonyl absorption due to acid groups at 1705 cm^{-1} confirms the completion of the reaction. ^1H-NMR spectrum (Figure 2), shows $-CH_3$ protons between the phenyl rings at 1.65 δ (E), $-CH_3$ protons bound to unsaturated double bonds at 2.00 δ (B), a pendant hydroxyl group between 2.10-2.80 δ (F), protons derived by reaction of the epoxy rings 3.70-4.00 δ (C), vinyl protons at 5.60 δ and 6.15 (A) and protons of the ring between 6.60 and 7.25 δ (D), confirm the structure of Bis-GMA.

The resins produced this way were used without further purification, since they were very viscous even at 90°C. The very small excess of methacrylic acid would react equally well during curing. For the curing reactions, modifiers (comonomers) were also added, along with an excess of initiator into the flask containing the Bis-GMA resin. The reactants were mixed well and cured at 160°C for 24 hours in RTV-silicone molds.

Table 1 shows the composition of the networks. All modifiers were used at a level of about 10 percent by weight. Sample 5 is a cycloaliphatic amine (PACM-20) cured Epon-828 and used for comparison. All products obtained after curing were transparent, with a slightly yellowish color.

Glass transition temperatures obtained by DSC are given in Table 2, together with other thermal transition data. As can be seen, the T_g values of free-radically cured networks are much higher than the amine cured epoxy network (Sample 5). On the other hand, in some of the modified systems there is a decrease in the transition temperature. This latter effect reflects a high level of miscibility and thus a random distribution of modifiers in the system; i.e., a "compatible" network. It is also possible to obtain microphase separated networks depending on the amount, reactivity, solubility parameter and molecular weights of the modifiers used (6).

TMA penetration curves are reproduced in Figure 3. Since the samples were very rigid and strong, it was necessary to have a load of 200 g during the experiments to achieve suitable penetration. As can be seen from the curves, the penetration is much less in Bis-GMA based networks than the amine cured epoxy network. This data suggests a higher modulus for these types of resins. On the other hand, depending on the type of modifier used, the level of penetration is seen to vary.

Styrene modification yields a stiffer, somewhat stronger network when compared with the unmodified Bis-GMA resin. This may be related to the steric hindrance in the cured resin provided by the aromatic ring of the polystyrene. This approach is also reported to enhance the chemical resistance of the network in various environments (4). By contrast, the penetration of 2-ethylhexyl acrylate and siloxane modified systems is larger, as might be expected in view of their flexible structures. On the other hand these modifiers may be useful in providing higher impact strength and crack resistant materials.

Thermal decomposition of the products were studied under nitrogen atmosphere by TGA. Percent weight loss versus temperature curves obtained are given in Figure 4. It is clear that Bis-GMA type of networks are much more stable to thermal degradation than the conventional epoxy network control. For example, at 400°C, where Sample 5 shows almost 50 percent loss in weight, the weight loss for the Bis-GMA network is less than 5 percent. Thermal stability, as expected, also depends on the modifier used and can be further improved by use of specific comonomers and/or external stabilizers.

The results on the dynamic mechanical behavior of the products are shown in Figures 5-7. Figure 5a and 5b give the loss tangent and storage and loss moduli against temperature for the unmodified Bis-GMA and epoxy networks respectively. In Figure 6, tanδ is plotted against temperature for the unmodified and modified Bis-GMA networks and Figure 7 gives the modulus-temperature curves for those systems. Numerical values of the transition temperatures are included in Table 2.

As can be seen from these figures, one observes principally two transitions with a possible additional shoulder in the upper transition for the free-radical cured Bis-GMA networks, these two principal transitions were also observed in TMA penetration curves (Figure 3). The former transition occurs between 80-110°C and the latter transitions are in the range of 190-220°C. On the other hand, amine cured epoxy network has only a single transition which lies between 160-190°C at the frequency investigated. It is known that in chain (co)polymerization of bis-unsaturated monomers, cyclization is important and this may be predominant at the onset of the reaction (11-13). This phenomenon is usually explained by chain flexibility and the relative probabilities of intra and intermolecular reactions of the active radicals with the pendant double bonds (14). The transition in the range 80-110°C may be due to these type of cyclization reactions of Bis-GMA. In fact, a linear poly(hydroxy ether) "phenoxy" resin also shows a loss peak and major glass transition around 110°C under the same conditions. Obviously, this point needs further experimental evidence and investigation. The transitions in the high temperature region reflect the three-dimensional network character. The principal peaks are also consistent with the T_g's determined by DSC. Table 2 contains all transition temperatures, obtained from DSC scans and from the inflection points of penetration and storage modulus versus temperature curves. Values obtained by the Rheovibron are a little higher, due to the nature of the experiment and the frequency used (110 Hz) during the measurements. The effect of the modifier on transition temperatures and modulus depends mainly on their molecular structure, as expected. Thus, styrene yielded higher glass transition and penetration temperatures compared with the siloxane and the acrylate modifier.

Stress-strain data on the networks are given in Table 3. Moduli and stresses at break are given in both kg/cm^2 and SI units. As may be seen, the unmodified Bis-GMA network has a somewhat higher modulus than the epoxy network, which is in accordance with other observations. The stress and elongation at break are somewhat smaller due to the high rigidity of the system, although end point differences are rather small. On the other hand, it is possible to alter the system by using different modifiers and improve some desired property. Styrene modification yields a stronger network with a substantially higher modulus and elongation at break. The increase in stress at break over that of the unmodified system is also fairly good (>35%). Siloxane and 2-ethylhexyl acrylate modifications, without affecting the modulus, show an increase in stress at break, from 255 to 376 and 394 kg/cm^2 and a small increase in in elongation at break, from 2% to 3 and 4% respectively. By changing the amount of modifiers and using a mixture of styrene and a rubber forming monomers, it may be possible to obtain improved stress-strain properties for these type of networks.

In conclusion, the Bis-GMA type of networks may have some very desirable properties, e.g. as coating materials. In order to further improve the properties, different initiators and curing conditions should be studied, including UV-initiation. It is also obvious that further investigation is needed to see the effects of changing the amount, type and molecular weight of the modifiers used. These parameters have been previously examined in order to optimize the overall properties in conventional epoxy resins (15,16). As mentioned earlier, cyclization may play an important role in these types of cross-linking reactions. Determination of the extractables (sol fraction) may be important if one wishes to provide resistance to different solvents and chemicals. Styrene modification seems to provide better overall properties for these networks, which has already been recognized in commercial formulations. When combined with proper rubbery vinyl monomers or oligomers, one may also achieve improved impact strength. Moreover, since these types of networks are widely used as coating materials, their surface properties can also be modified to produce an increased hydrophobicity and perhaps better properties such as wear and abrasion or even smaller friction coefficients by using various vinyl terminated siloxane oligomers, which we have already synthesized in our laboratories(17).

ACKNOWLEDGEMENT:

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REFERENCES

1. W. V. Breitigam and L. L. Brass, Tech. Bull., Shell Chem. Co., SC: 481-80.
2. J. E. Enos, R. L. Erratt, E. Francis and R. E. Thomas, Polym. Composites, 2, 53 (1981).
3. "Epocryl Resins 480", Tech. Bull., Shell Chem. Co., SC: 122-80.
4. "Fabricating with Epoxy Resins", Tech. Bull., Shell Chem. Co., (1980).
5. R. E. Toughsaent, D. A. Thomas and L. H. Sperling, J. Polym. Sci., Symp. No. 46, 175, (1974).
6. L. H. Sperling, Mod. Plast., Oct. 1981, p. 74.
7. L. H. Sperling, "Interpenetrating Polymer Networks and Related Materials", Plenum Press, New York, N.Y., 1981.
8. H. Lee and K. Neville, "Handbook of Epoxy Resins", p. 4-17, McGraw Hill, New York, (1967).
9. F. Svec, J. Labsky, L. Lanyova, J. Hradil, S. Plkorny, and J. Kalal, Angew. Macromol. Chemie, 87, 127 (1980).
10. D. Ades and M. Fontanille, J. Appl. Polym. Sci., 23, 11 (1979).
11. P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953.
12. H. Kast and W. Funke, Macromol. Chem., 180, 1335 (1979).
13. K. Dusek, Macromol. Chem., Supp. 2, 35 (1979).
14. K. Dusek, H. Galina, and J. Mikes, Polym. Bull., 3, 19 (1980).
15. J. N. Sultan and F. McGarry, Polym. Eng. Sci., 13, 29 (1973).
16. E. H. Rowe, A. R. Siebert and R. S. Drake, Mod. Plast., 49, 110 Aug. 1970.
17. J. E. McGrath et al., Organic Coatings and Plastics Preprints, 23(1), 397 (1982).
18. R. J. Jackson, U.S. 4,303,579 (to Shell Oil Co.), Dec. 1981, CA 96,69972t (1982).

TABLE 1

Synthesis of Bis GMA Networks: Investigation of Three Modifiers

Sample #	Modifier	Modifier Percent (by weight)
1	--	--
2	Styrene	10.5
3	2-Ethylhexyl acrylate	10.7
4	Vinyl terminated disiloxane	10.9
5*	Epon 828 + PACM-20	--

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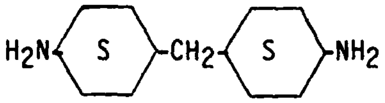


cured Epon-828

TABLE 2

Thermal Transition Behavior of Methacryloxy Cured Networks

Sample #	T_g[a] (°C)	Tp[b] (°C)	Ti[c] (°C)
1	191	117,198	92,224
2	189	112,183	--
3	179	106,180	81,220
4	179	89,184	78,213
5[d]	148	152	181

(a) Obtained by DSC, heating rate 10°C/min

(b) Inflection points in penetration curves

(c) Inflection points in storage modulus-temperature curves

(d) EPON 828/PACM 20 diamine control

TABLE 3

Stress-Strain Properties of Methacryloxy Cured Networks

Sample #	E (kg/cm^2)	E (GPa)	σ_B (kg/cm^2)	σB (MPa)	εB (%)
1	10,500	1.03	255	25	2
2	14,500	1.42	350	34	3
3	10,800	1.06	376	37	3
4	9,800	0.96	394	39	4
5	8,000	0.80	502	49	6

CAPTIONS FOR FIGURES

Figure 1. IR Spectrum of Bis-glycidyl Methacrylate of Bisphenol A (Bis-GMA) Resin

Figure 2. ^{1}H-NMR Spectrum of Bis-GMA Resin

Figure 3. Penetration Curves for Methacryloxy Cured Networks (Load 200 g, Heating Rate 10°C/min)

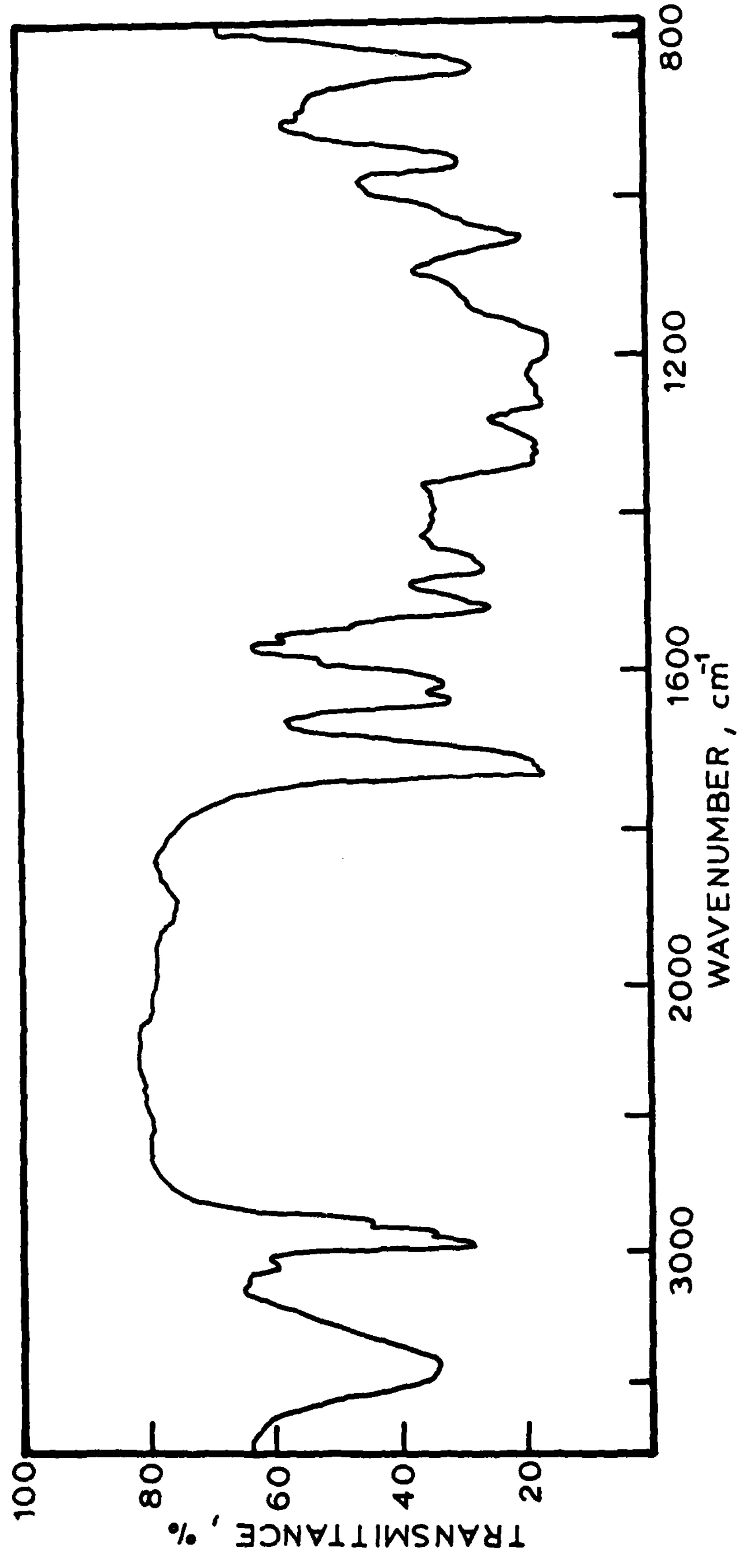
Figure 4. Percent Weight Loss Versus Temperature of Methacryloxy Cured Networks (Heating Rate 20°C/min)
(◑ = sample 1, ● = sample 2, ○ = sample 4, ◒ = sample 5)

Figure 5a. Tanδ Versus Temperature Curves for Epoxy and Bis-GMA Based Networks (Frequency 110 Hz)
(○ = sample 1, ● = sample 5)

Figure 5b. Storage and Loss Modulus Versus Temperature Curves for Bis-GMA and Epoxy Based Networks
(○ = sample 1, ● = sample 5)

Figure 6. Dynamic Mechanical Behavior of Bis-GMA Based Networks (Frequency 110 Hz)
(○ = sample 1, ● = sample 3, ◑ = sample 4)

Figure 7. Storage and Loss Modulus Versus Temperature Curves for Bis-GMA Based Networks
(○ = sample 1, ● = sample 3, ◑ = sample 4)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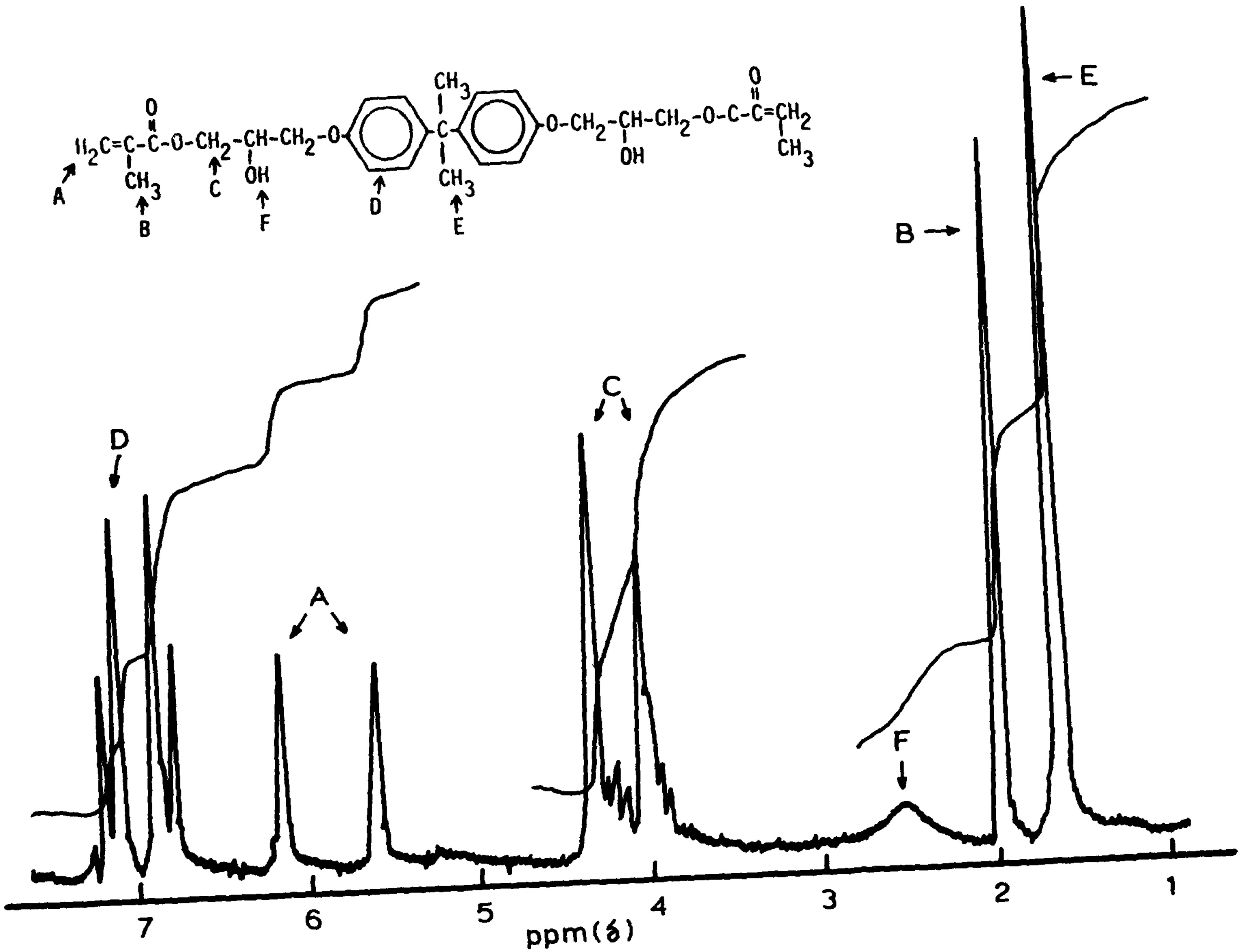
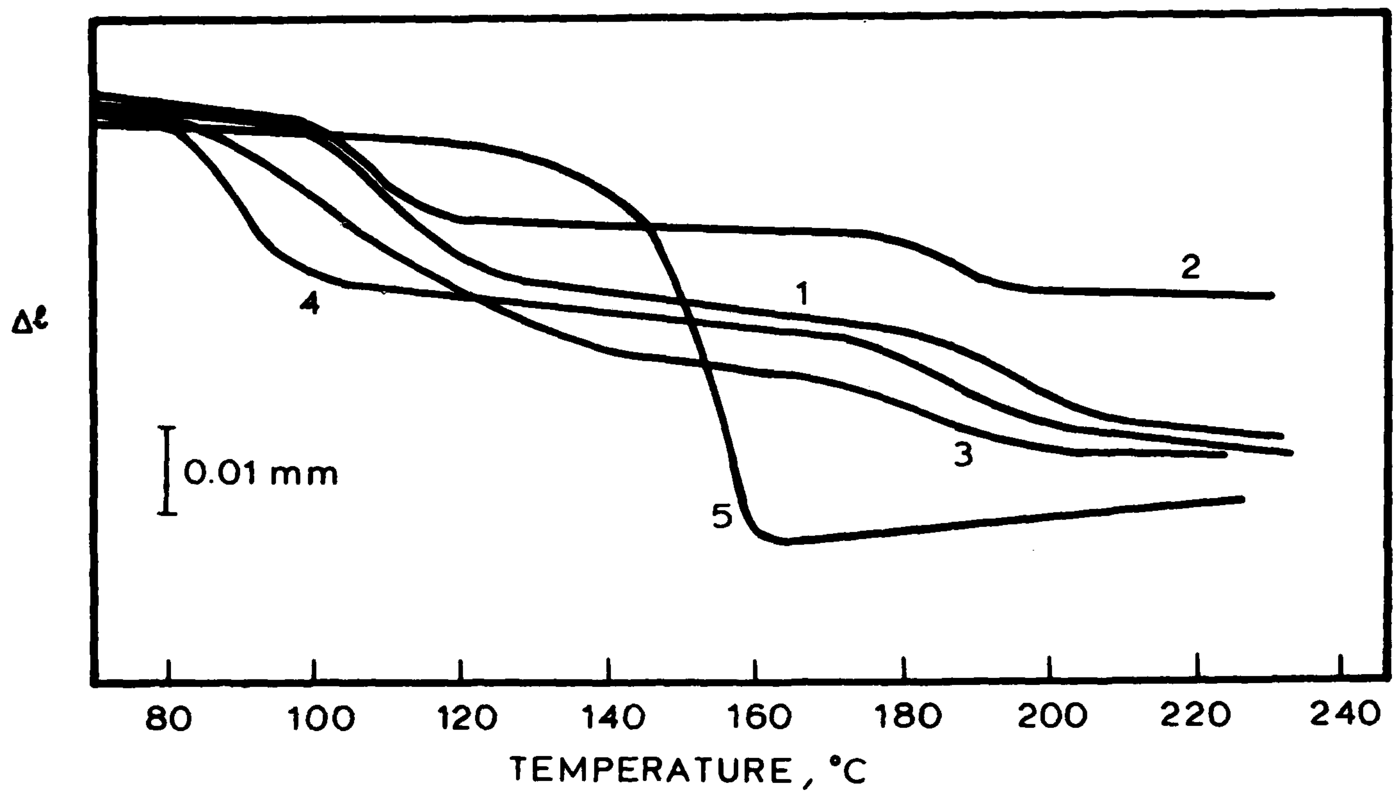


NMR SPECTRUM OF BIS-GMA

Δℓ
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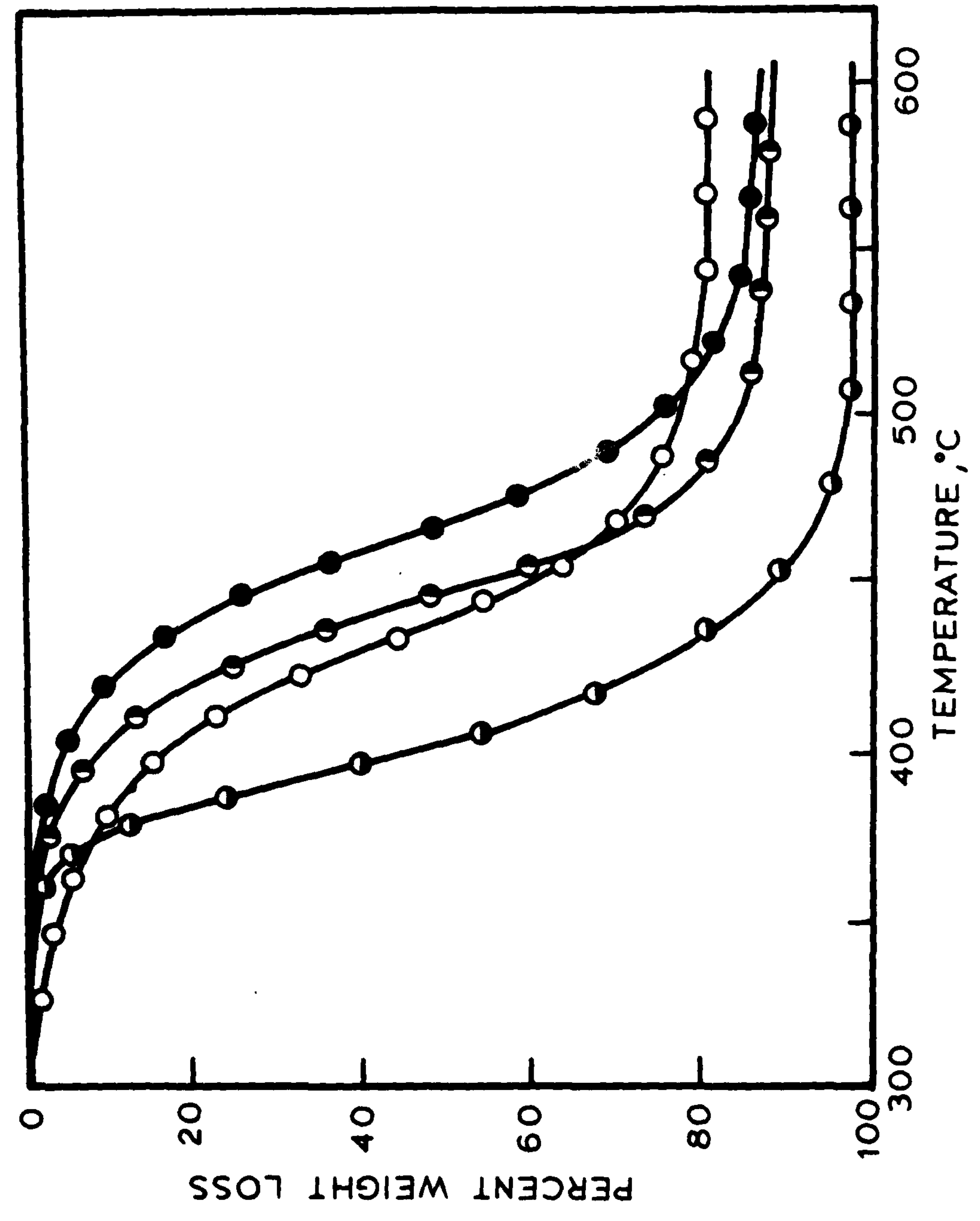
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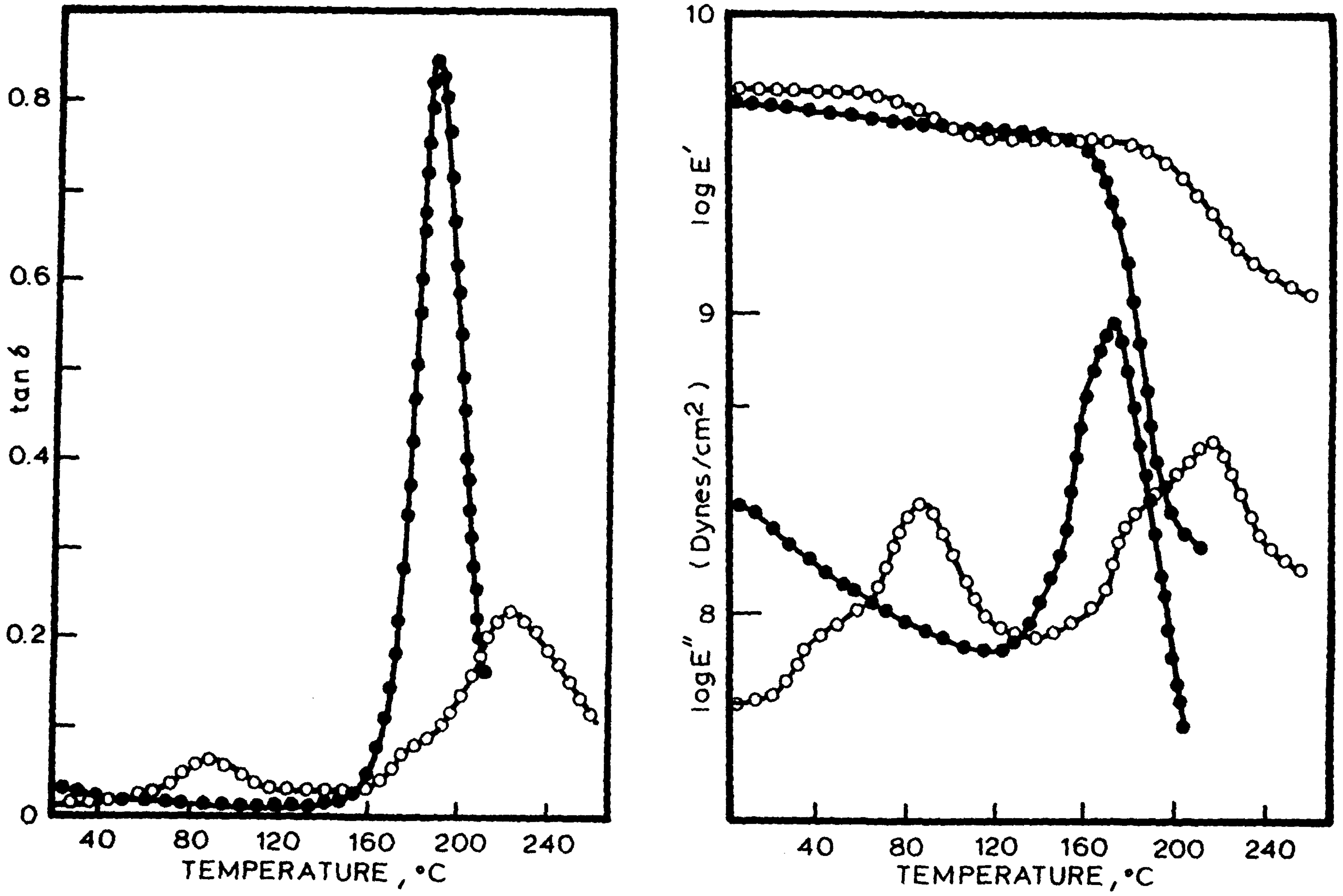
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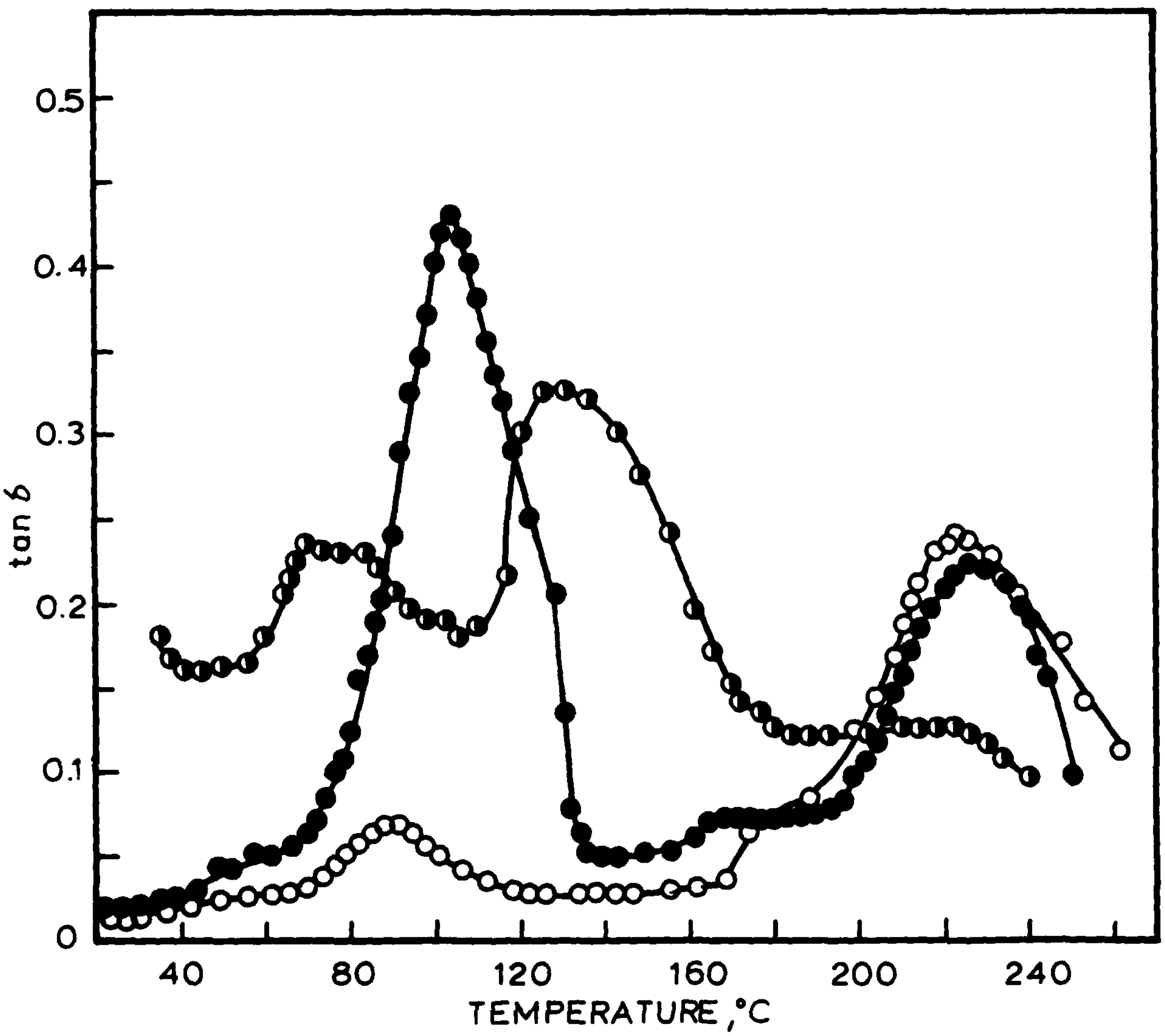
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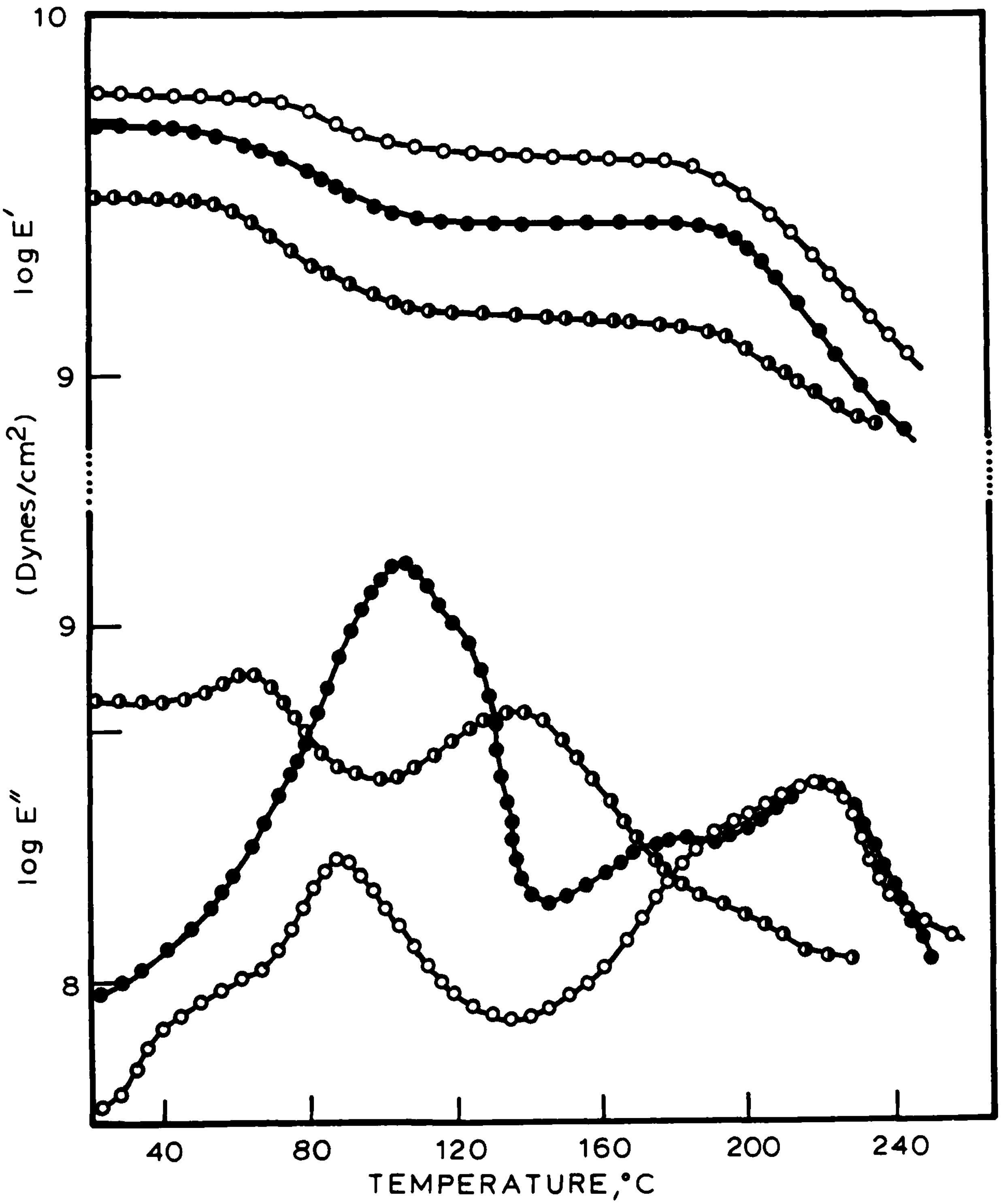
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