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UV-CURABLE POLYURETHANE-METHACRYLATE CO-NETWORKS AND INTERPENETRATING NETWORKS

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ABSTRACT

Castor oil was reacted in varying ratios with β -isocyanatoethyl methacrylate to form a liquid urethane-methacrylate prepolymer. This prepolymer was then cured using ultra-violet radiation to form a series of base networks or with various methacrylates to form a series of co-networks. By swelling the base networks with the appropriate methacrylate monomers, semi- and full-interpenetrating networks (IPNs) were also prepared with similar compositions. All of the materials formed transparent films. Results of swelling experiments, dynamic mechanical analysis, differential scanning calorimetry, and small angle x-ray scattering are reported.

INTRODUCTION

Interpenetrating polymer networks (IPNs) exhibit a variety of interesting properties and have been the subject of recent reviews^{1,2}. An IPN may be defined as "a combination of two polymers in network form, at least one of which is synthesized and/or crosslinked in the presence of the other"¹. This method of forming the networks allows the morphology of the resultant material to be controlled. In particular, the extent to which the component networks phase-separate is limited.

One of the more useful properties of IPNs is their damping behavior^{3,4}. Homopolymers damp vibrations over a relatively narrow temperature range near their glass-transition temperature, T_g . Phase-separated multicomponent polymers exhibit good damping near the

T_g s of the constituent polymers, but do not damp well at other temperatures⁵. The limited phase-separation caused by the unique microstructure of IPNs broadens the glass transition regions of the component networks and merges them into a single transition covering a wide temperature range^{3,4}. It is this broad T_g which makes IPNs a strong candidate for high-damping applications.

A series of UV-curable polyurethane-acrylates with various soft segments, diisocyanates, and reactive diluents have been previously investigated in our laboratories⁶⁻⁹. In this investigation, a new series of castor oil based polyurethane-acrylates were synthesized by reacting castor oil with varying amounts of β -isocyanatoethyl methacrylate with a series of other methacrylates as diluents. Although castor oil as a urethane component and in IPNs is not new¹⁰⁻¹³, it was chosen for this study for several reasons. The low molecular weight of the prepolymers results in low viscosity, making it possible to use these materials as solventless coatings. The final materials are transparent films which exhibit low toxicity, and the castor oil exhibits good compatibility with both hydrophobic and hydrophilic components. One of the major interests, as indicated above, is the high-damping characteristics of these materials.

In this contribution, castor oil and β -isocyanatoethyl methacrylate were reacted in varying ratios to form a series of liquid urethane-methacrylate prepolymers. These prepolymers were then cured with a series of methacrylates using ultra-violet radiation to form co-networks. Base polymers were formed by curing the prepolymer without an additional methacrylate. Semi-IPNs and full-IPNs were prepared by



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swelling the base networks with methyl methacrylate, and propylene glycol dimethacrylate for the full-IPNs, and then curing a second time with UV radiation. All of the materials were obtained as transparent films. Results of swelling experiments, dynamic mechanical analysis, differential scanning calorimetry, and small-angle x-ray scattering are reported.

EXPERIMENTAL

Castor oil was obtained from Aldrich Chemical Co. and was dehydrated under vacuum at 70 °C for 24 hours before use. The β -isocyanatoethyl methacrylate (IEM) was obtained from Polysciences and was used as received. The reactive diluents were a series of methacrylates, obtained from Aldrich Chemical Co. containing inhibitor, and were used as received. Prepolymers were synthesized by slowly adding the IEM to the dried castor oil with stirring, maintaining the temperature below 50 °C to avoid appreciable thermal polymerization of the acrylate (Figure 1). The mixture was allowed to stand overnight, and complete reaction of the isocyanate was confirmed by infrared spectroscopy. Prepolymers of different compositions were formed by varying the ratio of IEM to castor oil.

Co-networks were formed by adding a reactive diluent and 0.6 wt% 2,2'-diethoxyacetophenone as a photoinitiator. The reactive diluents were: methyl methacrylate (MMA), ethyl methacrylate (EMA), hydroxyethyl methacrylate (HEMA), butyl methacrylate (BMA), lauryl methacrylate (LMA), and iso-bornyl methacrylate (iBMA). Base networks were also formed by curing the prepolymer with no reactive diluent. The mixture

of prepolymer, photoinitiator, and reactive diluent was poured onto poly(ethylene terephthalate) (PET) film and covered with another piece of PET film to make a uniform thickness. The sample was exposed to UV light from one side using a bank of 20 W mercury lamps ($\lambda=365$ nm) as the radiation source. An irradiation time of 30 minutes was found to completely cure the samples. After UV-curing, all samples were dried under vacuum at 60-70 °C for at least 12 hours to remove any unreacted diluent. All samples were transparent to visible light.

Semi-interpenetrating networks (semi-IPNs) were formed by swelling the base networks with a mixture of reactive diluent and 0.6 wt% photoinitiator and curing by UV radiation. In a similar manner, full-IPNs were formed by swelling the base networks with a mixture of reactive diluent, 2 wt% propylene glycol dimethacrylate as a crosslinker for the second network, and 0.6 wt% initiator. Equilibrium swelling was achieved in less than four hours. The swollen films were again sandwiched between two pieces of PET film and were exposed to UV radiation for 5 minutes. The samples were postcured at 70 °C under vacuum overnight. A description of the materials which were synthesized for this investigation is given in Table 1.

Dynamic mechanical data were obtained using a computer controlled Rheovibron DDV-II-C. Data were taken from -50 °C to 200 °C at a frequency of 110 Hz and at a heating rate of 2 °C per minute.

Differential scanning calorimetry (DSC) thermograms were recorded from -130 °C to 200 °C using a Perkin-Elmer DSC 2 at a heating rate of 20 °C per minute. The data processing unit allowed automatic baseline subtraction and normalization of the thermograms by sample weight.

Swelling measurements were made by soaking the samples in solvent until an equilibrium weight was achieved (2 to 4 days). Weight measurements were made by blotting the samples dry and immediately placing them into a pre-tared capped vial. The swelling solvent was then removed by heating the samples to 60 °C under vacuum until equilibrium weight was again achieved. The reported swelling percentages were determined from the equilibrium swollen weight and the final equilibrium dried weight to account for solvent extraction and sample loss due to cracking in some samples.

Small-angle x-ray scattering (SAXS) patterns were obtained using a modified compact Kratky camera. X-rays were generated by an Elliot GX-21 rotating anode operating at 30 kV accelerating potential and 40 mA emission current. The scattered x-rays were detected by a one-dimensional position sensitive detector and associated electronics. The x-rays were filtered by nickel foil and a pulse height discriminator was used in the detector electronics to limit the x-rays to a predominant wavelength of 0.1542 nm ($\text{CuK}\alpha$). Corrections were made to the data to take into account detector sensitivity, detector linearity, detector dark current, parasitic scattering, and sample transmittance. Relative intensity data were converted to absolute intensity using a Lupolen polyethylene standard. An experimentally measured slit-length weighting function convoluted with a function which accounted for a finite detector window was used to desmear the data by the iterative method of Lake.

RESULTS AND DISCUSSION

Figure 2 shows the dynamic mechanical data for two of the base networks. As the crosslink density is increased due to a higher IEM to castor oil ratio, the high temperature storage modulus (E') plateau is increased, and the glass transition temperature (T_g) (the peak in the loss modulus, E'') moves to a higher temperature.

Figure 3 shows the dynamic mechanical data for the co-networks. These figures demonstrate that both the T_g and the storage modulus plateau are affected by sample composition, but the two do not follow the same trends. The position and breadth of the glass transition depends on the T_g of the component materials and the degree to which the components are phase separated. The storage modulus is more strongly affected by the crosslink density. The differences in the storage modulus plateau are probably due to differences in the average molecular weight between crosslinks. If the reactivity ratio of a methacrylate causes it to react with itself rather than the pendant methacrylate on the prepolymer, a lower crosslink density will result.

The effect of sample structure on the dynamic mechanical properties of the networks is shown in Figure 5. In going from the base network to the co-network to the semi-IPN to the full-IPN, the T_g is seen to increase. The breadth of the glass transition as indicated by the breadth of the peak in E'' is also seen to increase for the two IPN samples. The high temperature storage modulus plateau is lower for the co-network than it is for the base network. This reflects the lower crosslink density, or higher molecular weight between crosslinks, which exists in the co-network. The higher molecular weight between

crosslinks is due to the poly(methyl methacrylate) part of the co-network. The fact that the storage modulus plateau of the semi-IPN is the same as that of the base network indicates it is the base network component of the semi-IPN which is responsible for the structural integrity of the sample at higher temperatures. The higher storage modulus plateau of the full-IPN is due to the additional load bearing capacity of the second methacrylate network.

The dynamic mechanical data for the semi-IPNs are shown in Figure 6. These data basically show the same trends as the base networks. As the crosslink density of the base network component is increased, the storage modulus plateau and the T_g increase. The dynamic mechanical data from the full-IPNs are shown in Figure 7. Sample CAS-IEM-1.5/PMMA Full-IPN broke at about 90 °C during testing and was not retested. Again the same trend in T_g is seen. The trend in the storage modulus plateau is not as evident in this series of materials. The reasons for this are not clear, but one should recall that the storage modulus plateau has contributions from both networks.

An example of one of the DSC thermograms is shown in Figure 8. A glass transition is seen near -10 °C. In general, though, the glass transitions in these materials were broad and difficult to find. When present, the T_g from DSC thermograms occurred at a lower temperature than that determined from dynamic mechanical measurements.

Figure 9 shows the results of swelling experiments on CAS-IEM-3.0/PMMA Full-IPN. The swelling solvents shown are all moderately hydrogen-bonding. From the plot it is evident that the solubility parameter of this sample is near $9 \text{ (cal cm}^{-3})^{1/2}$. The other

samples undoubtedly have different solubility parameters due to their varying compositions. Dioxane was chosen as the solvent for the other swelling experiments because the tetrahydrofuran caused this sample to break up. The dioxane also gave a reasonable balance between low solvent volatility at room temperature, which allowed for relatively easy sample weight determination, and ease of solvent removal under vacuum at 60 °C.

Figure 10 shows the results of swelling experiments in dioxane for several of the materials. As expected, the swelling percentage decreases as the crosslink density increases (increasing IEM/castor oil ratio). The generally higher swelling percentage of the full-IPNs is due to the fact that the solubility parameter of the methacrylate network is nearer to the solubility parameter of the solvent, 1,4-dioxane ($10.0 \text{ (cal cm}^{-3})^{1/2}$), than that of the base network is. (The solubility parameter of methyl methacrylate is reported¹⁴ to be in the range of 9.0 to $9.5 \text{ (cal cm}^{-3})^{1/2}$.) The reason that CAS-IEM-1.5/PMMA Full IPN swells less than the base network is not clear, but as seen in Table 1, this sample contains only 4 wt% methacrylate network.

An example of small-angle x-ray scattering from three of the samples is shown in Figure 11. There is only a broad low intensity peak for any of the materials indicating that these materials are phase separated with weak electron density contrast between the phases. Though it is not unexpected that the electron density of the castor oil phase is similar to that of the methacrylate phase, the lack of any sharp features in the SAXS pattern indicates that there is not a significant amount of order within these materials. Note that the phase

separation is present even for the base network and that the addition of the second component does not significantly change the scattering pattern. This indicates that the poly(methyl methacrylate) component is in intimate contact with the base network.

SUMMARY

Series of polyurethane-methacrylate base networks, co-networks, semi-IPNs and full-IPNs have been synthesized. These materials were obtained as transparent films and were characterized by swelling experiments, dynamic mechanical analysis, differential scanning calorimetry, and small-angle x-ray scattering.

As the crosslink density was increased within each of the base network, semi-IPN, and full-IPN series: a higher high temperature storage modulus plateau was observed; the T_g moved to higher temperature; the $\tan \delta$ (or E'') peak narrowed; and the swelling percentage decreased. All of these results are due to the higher crosslink density and fewer dangling chains within the networks which result from a higher IEM to castor oil ratio in the prepolymer.

Both of the IPN series of materials exhibit a higher T_g and a broader loss peak than the corresponding co-network of similar composition. At the same time, however, small-angle x-ray scattering indicates that the basic morphology of the IPN materials is relatively unchanged from that of the base networks. Both of these results are due to the interpenetrating structure of the materials. The base network cannot change its morphology when the second component is introduced to make the IPN materials. Since the methyl methacrylate swells the base

networks well, it polymerizes in intimate contact with the base network.

The high temperature storage modulus plateau of a full-IPN is higher than those of the corresponding semi-IPN or base network which are in turn higher than that of the corresponding co-network. This is because the full-IPN, semi-IPN and base network all have the same base network component and the full-IPN has the additional methacrylate network to bear loads at higher temperatures. The co-network has a higher average molecular weight between crosslinks and so has a lower storage modulus plateau.

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Sample	IEM/CAS Mole Ratio	Weight Percentage IEM&CAS	
CAS-IEM-3.0-0	3.0	100	] Base networks
CAS-IEM-2.5-0	2.5	100	
CAS-IEM-2.0-0	2.0	100	
CAS-IEM-1.5-0	1.5	100	
CAS-IEM-2.5/MMA Co-network	2.5	86	] Co-networks
CAS-IEM-3.0/HEMA Co-network	3.0	80	
CAS-IEM-3.0/IsobornylMA Co	3.0	80	
CAS-IEM-3.0/LMA Co-network	3.0	80	
CAS-IEM-3.0/EMA Co-network	3.0	80	
CAS-IEM-3.0/PMMA Semi-IPN	3.0	82	] Semi-IPNs
CAS-IEM-2.5/PMMA Semi-IPN	2.5	86	
CAS-IEM-2.0/PMMA Semi-IPN	2.0	87	
CAS-IEM-1.5/PMMA Semi-IPN	1.5	88	
CAS-IEM-3.0/PMMA Full-IPN	3.0	86	] Full-IPNs
CAS-IEM-2.5/PMMA Full-IPN	2.5	86	
CAS-IEM-2.0/PMMA Full-IPN	2.0	87	
CAS-IEM-1.5/PMMA Full-IPN	1.5	96	

FIGURE CAPTIONS

Figure 1 - Reaction to form the prepolymer used in making all subsequent materials. The ratio of IEM to castor oil was varied from 1.5 up to 3 (shown).

Figure 2 - Dynamic mechanical data from two of the base networks. In all plots of dynamic mechanical data, the upper curves are the storage modulus (E') while the lower curves are the loss modulus (E'') or tangent δ .

Figures 3a and 3b - Dynamic mechanical data from the methacrylate co-networks.

Figure 4 - Dynamic mechanical data from the series of materials formed from the prepolymer with a 2.5:1 ratio of IEM to castor oil.

Figure 5 - Dynamic mechanical data from the PMMA Semi-IPN materials.

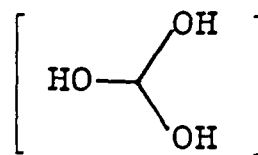
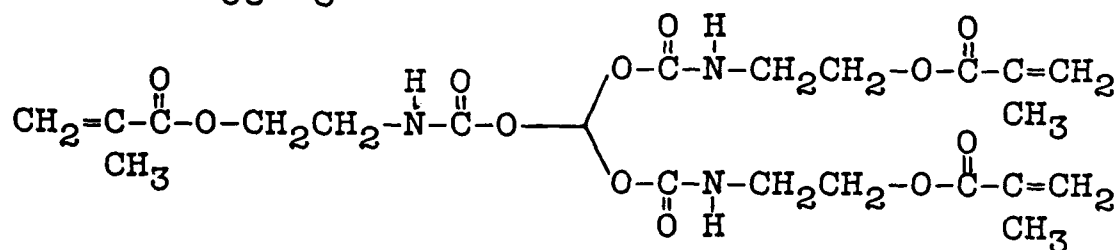
Figure 6 - Dynamic mechanical data from the PMMA Full-IPN materials.

Figure 7 - DSC thermogram from CAS-IEM-1.5/PMMA Full-IPN. The T_g is seen near -20°C for this material, but was difficult to observe^g in general.

Figure 8 - Small-angle x-ray scattering from the CAS-IEM-3.0 networks.

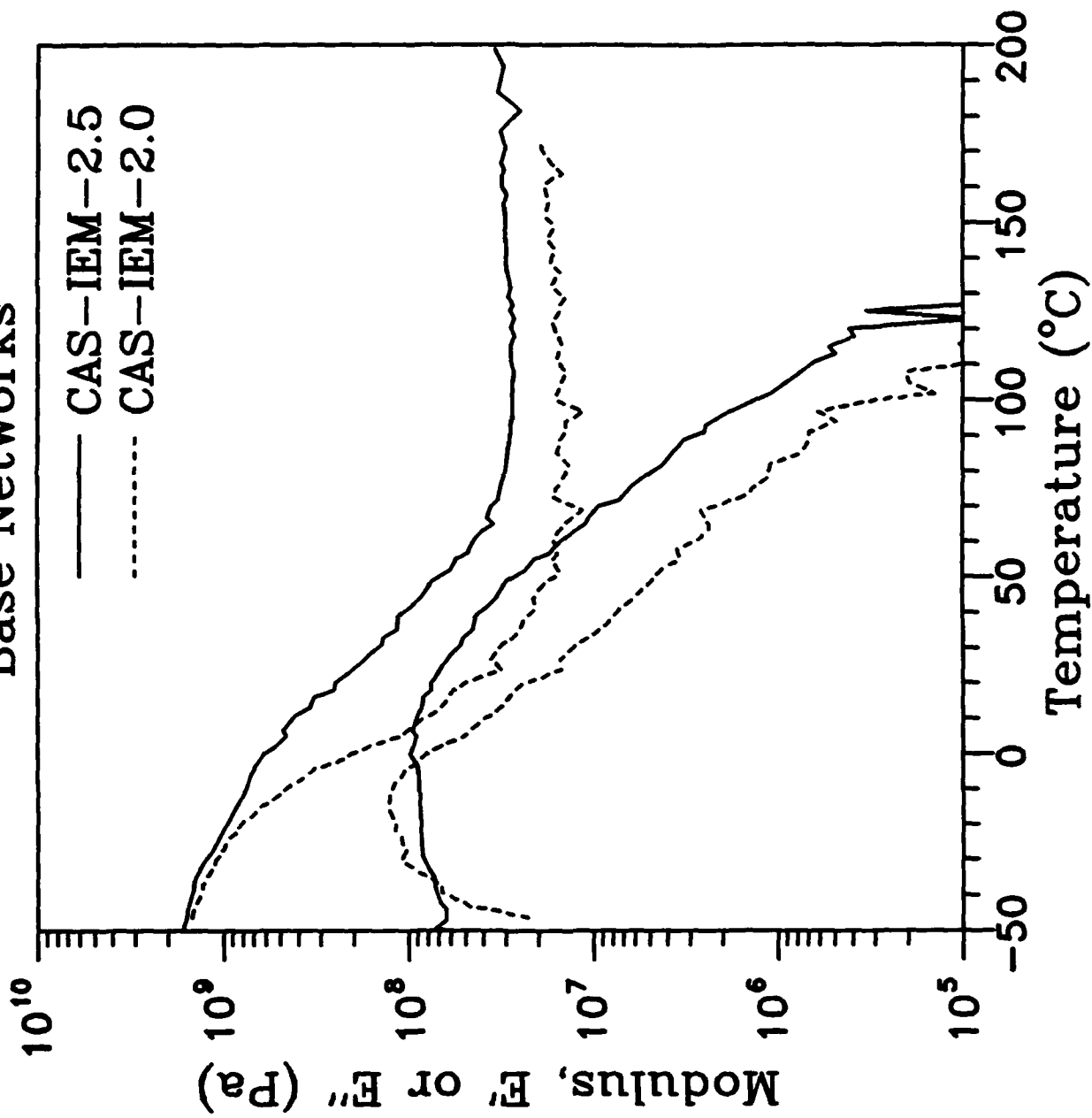
Figure 9 - Swelling percentage of CAS-IEM-3.0/PMMA Full-IPN in a series of moderately hydrogen bonding solvents of varying solubility parameter.

Figure 10 - Swelling percentage of networks in 1,4-dioxane.

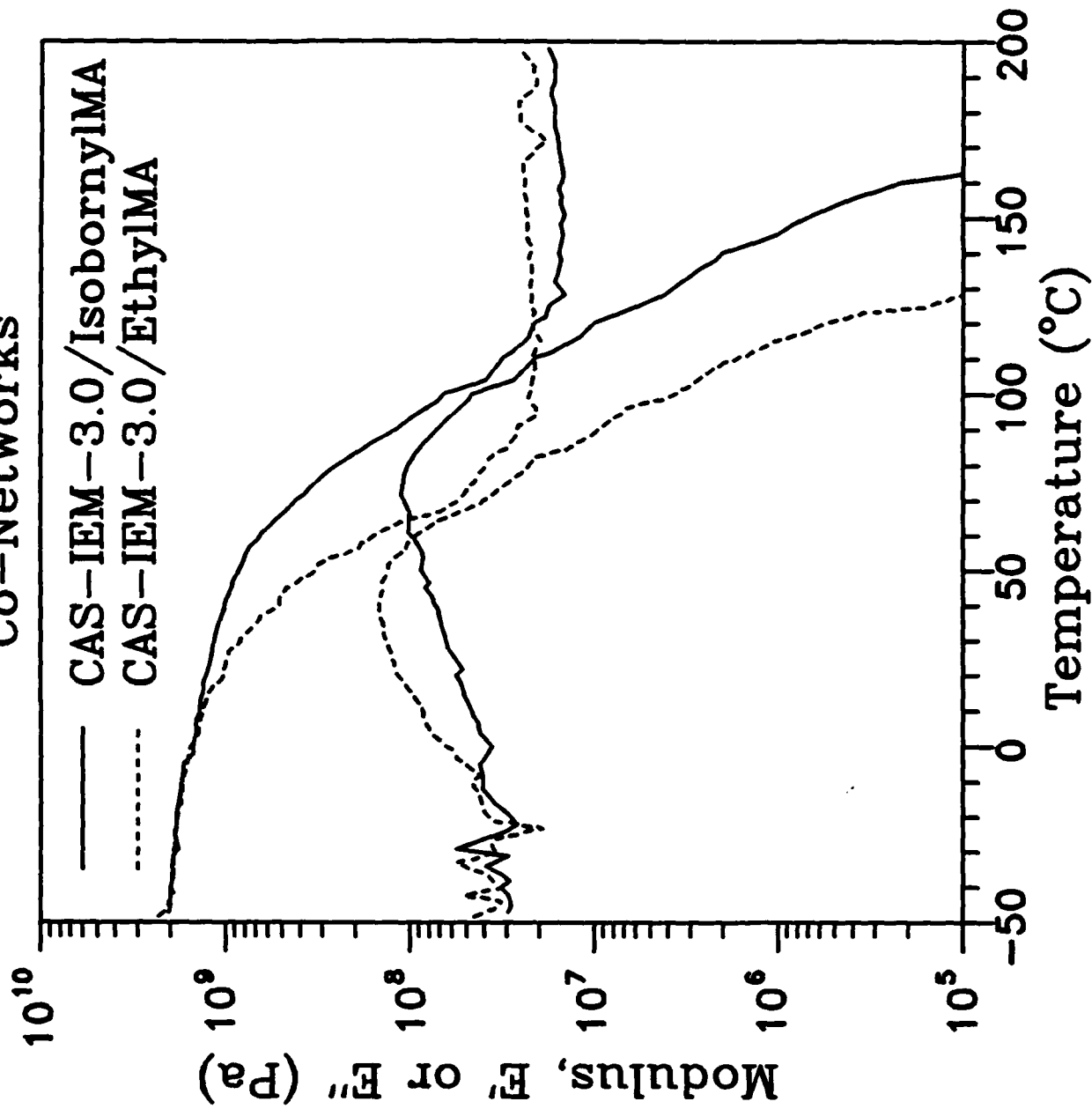
$$\begin{array}{c} \text{CH}_2\text{-O-C(=O)-(CH}_2)_7\text{-CH=CH-CH}_2\text{-CH(OH)-(CH}_2)_5\text{-CH}_3 \\ | \\ \text{CH}_2\text{-O-C(=O)-(CH}_2)_7\text{-CH=CH-CH}_2\text{-CH(OH)-(CH}_2)_5\text{-CH}_3 \\ | \\ \text{CH}_2\text{-O-C(=O)-(CH}_2)_7\text{-CH=CH-CH}_2\text{-CH(OH)-(CH}_2)_5\text{-CH}_3 \end{array}$$

$$\text{CH}_2=\underset{\text{CH}_3}{\text{C}}-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{O}-\text{CH}_2\text{CH}_2-\text{N}=\text{C}=\text{O}$$
$$\text{CAS} + 3 \text{ IEM} \xrightarrow[50^\circ \text{C}]{\text{Stannous Octoate}}$$


Prepolymer

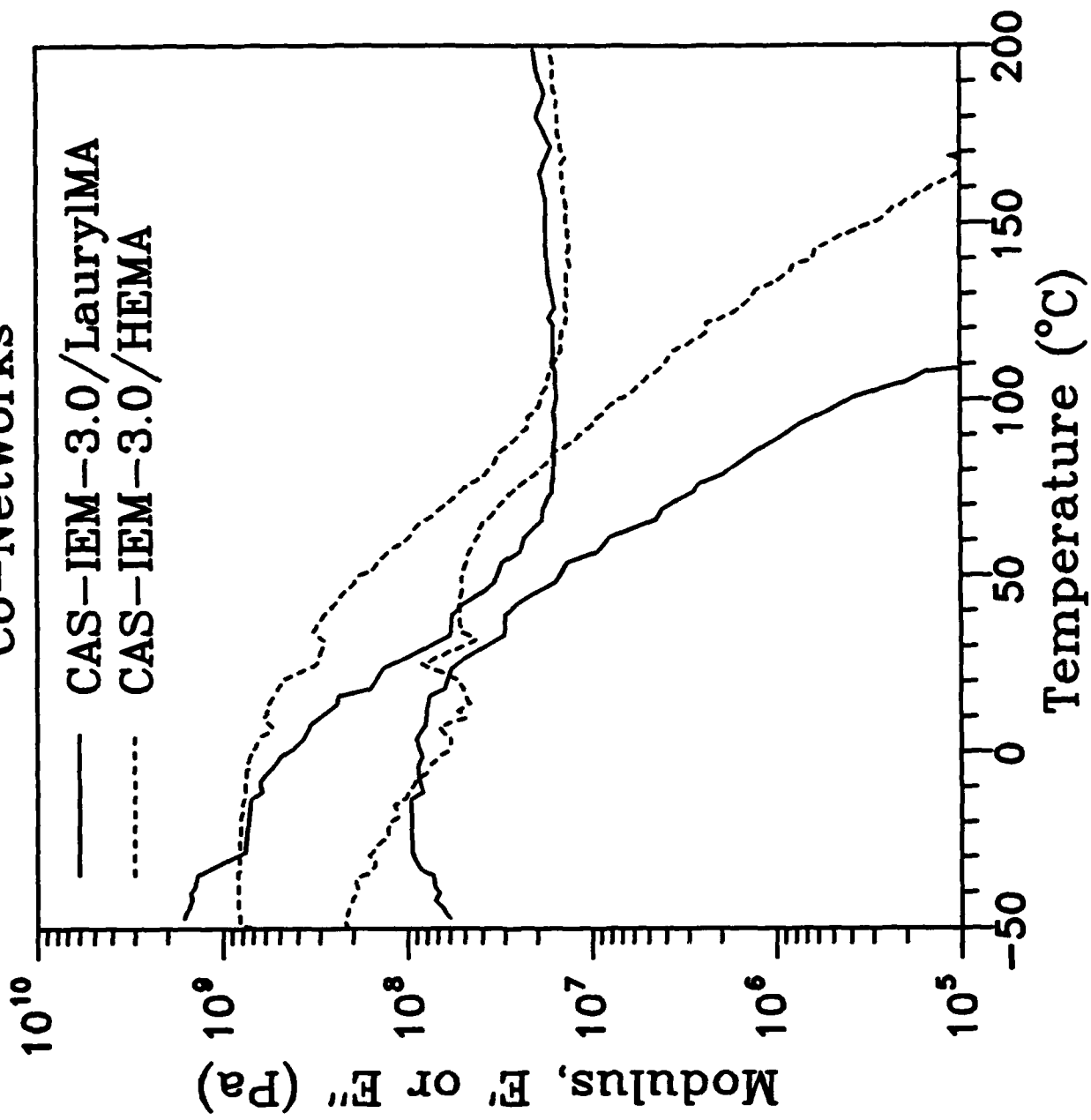
Base Networks



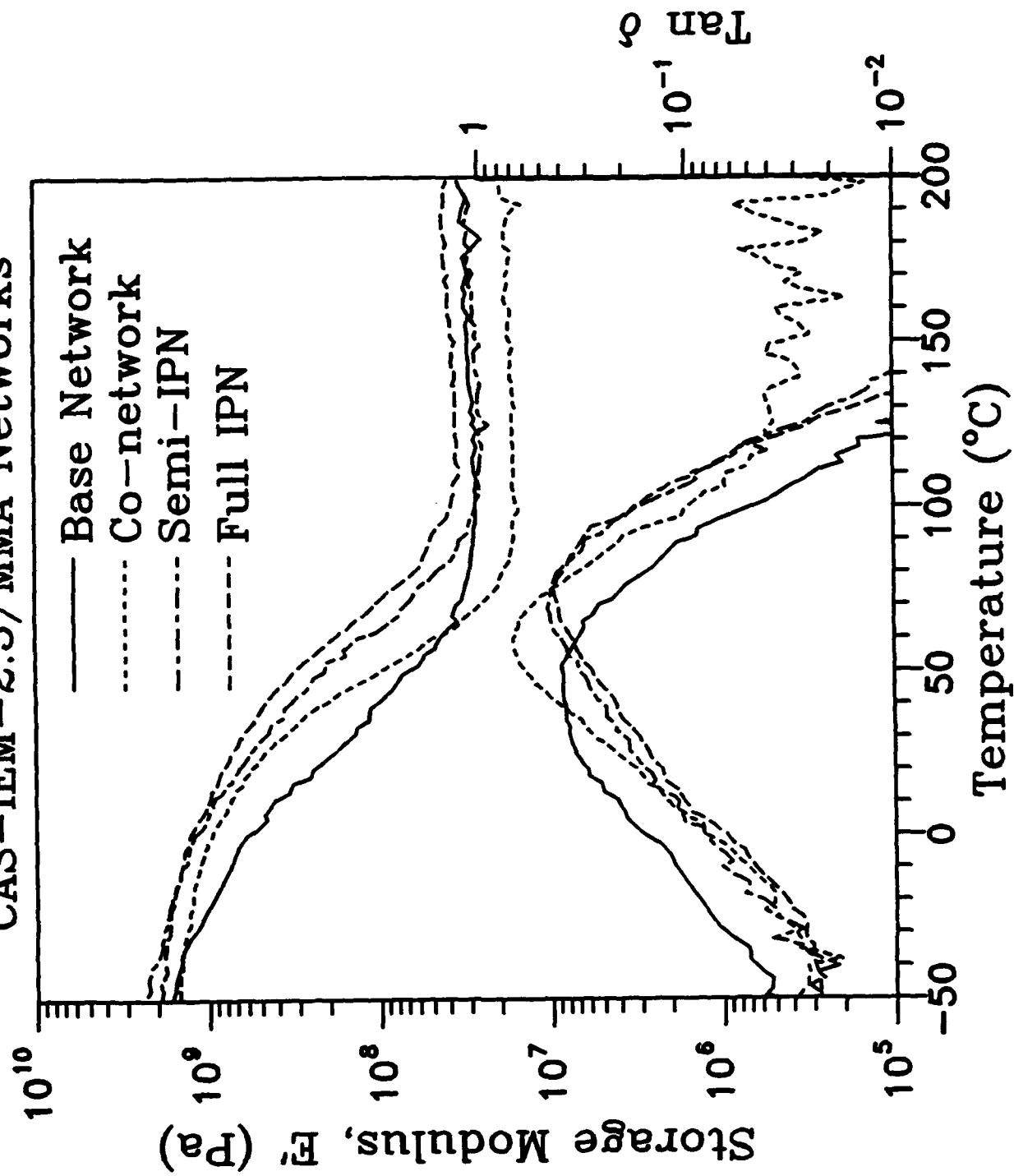
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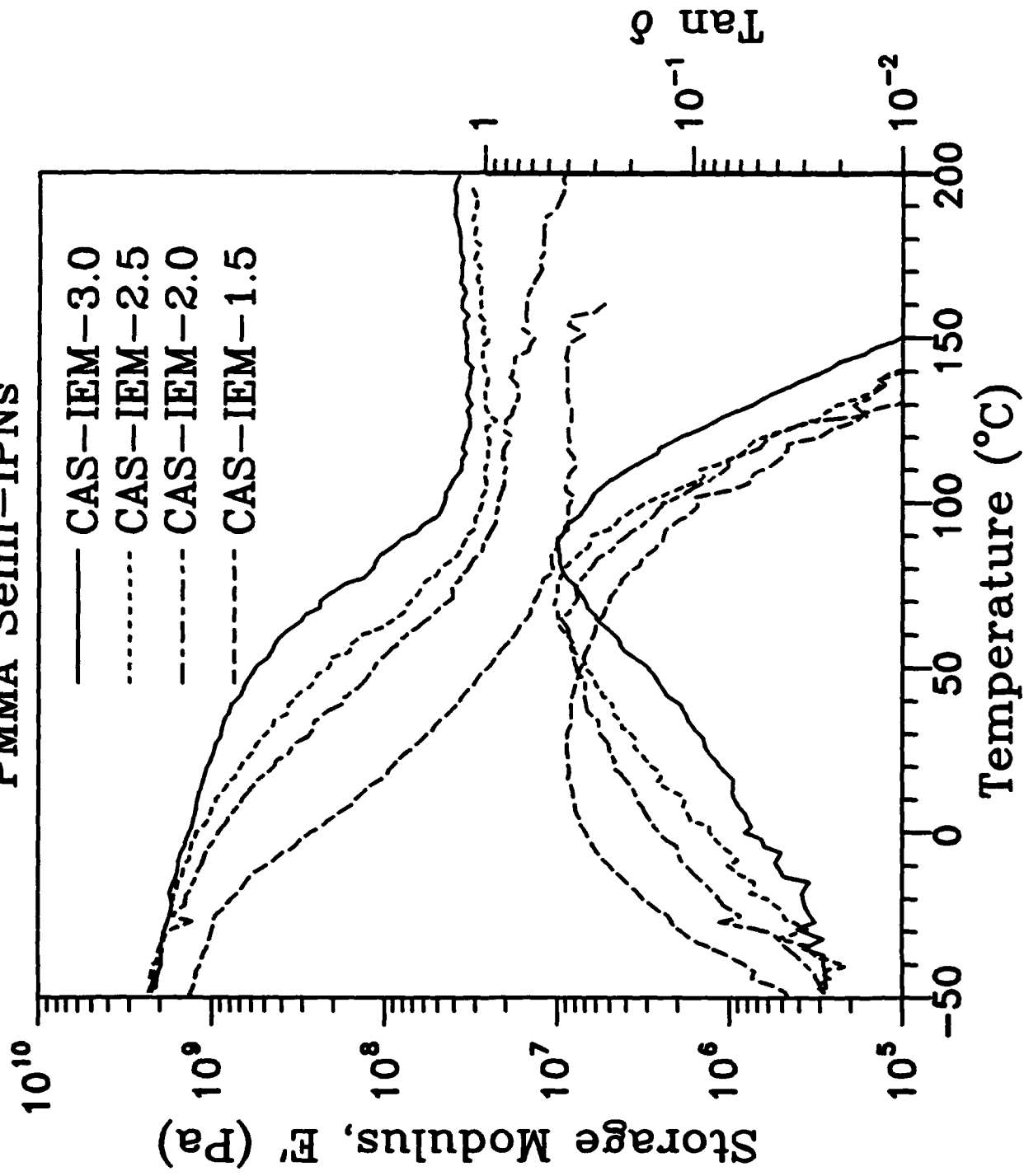
Co-Networks



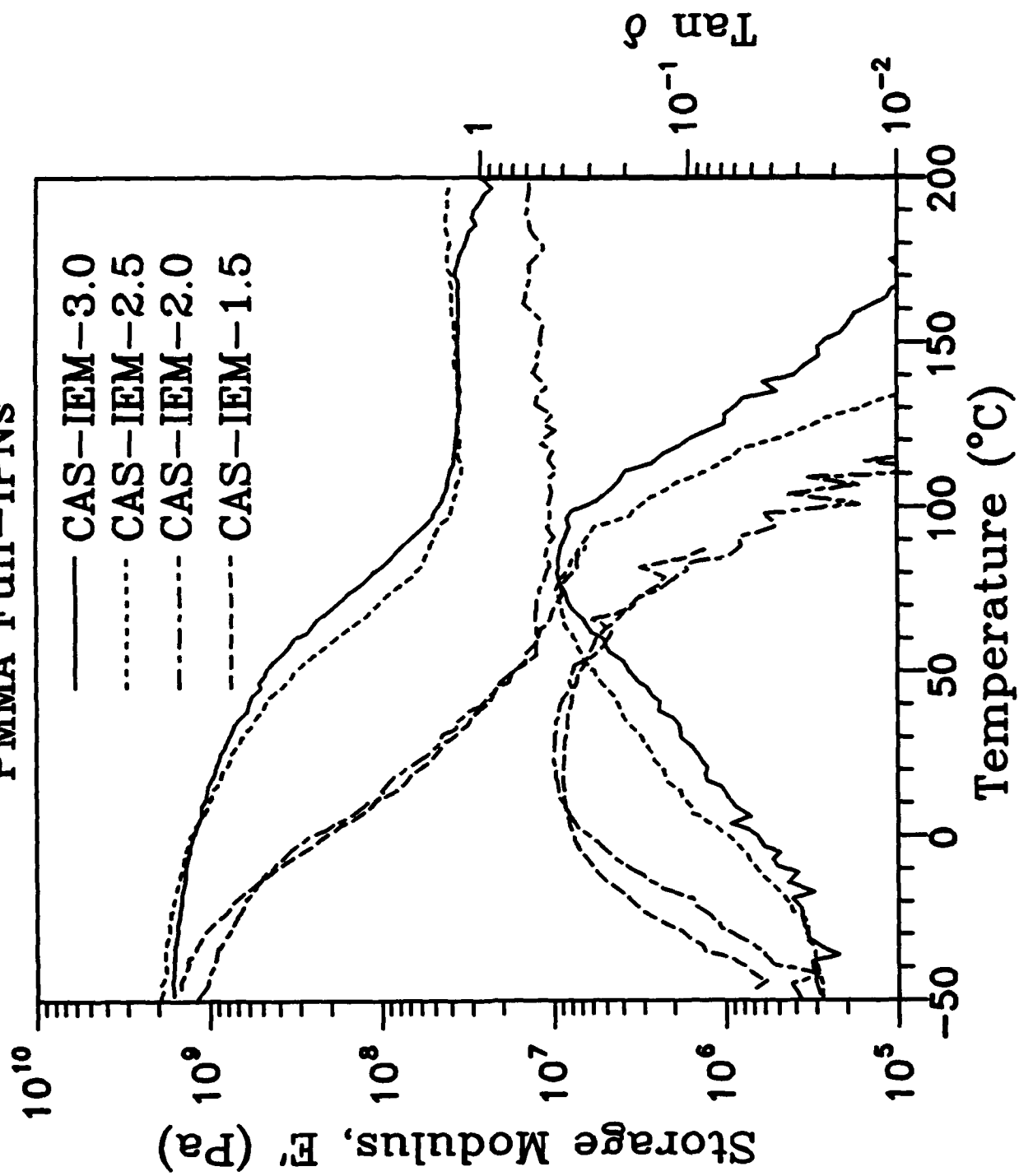
CAS-IEM-2.5/MMA Networks



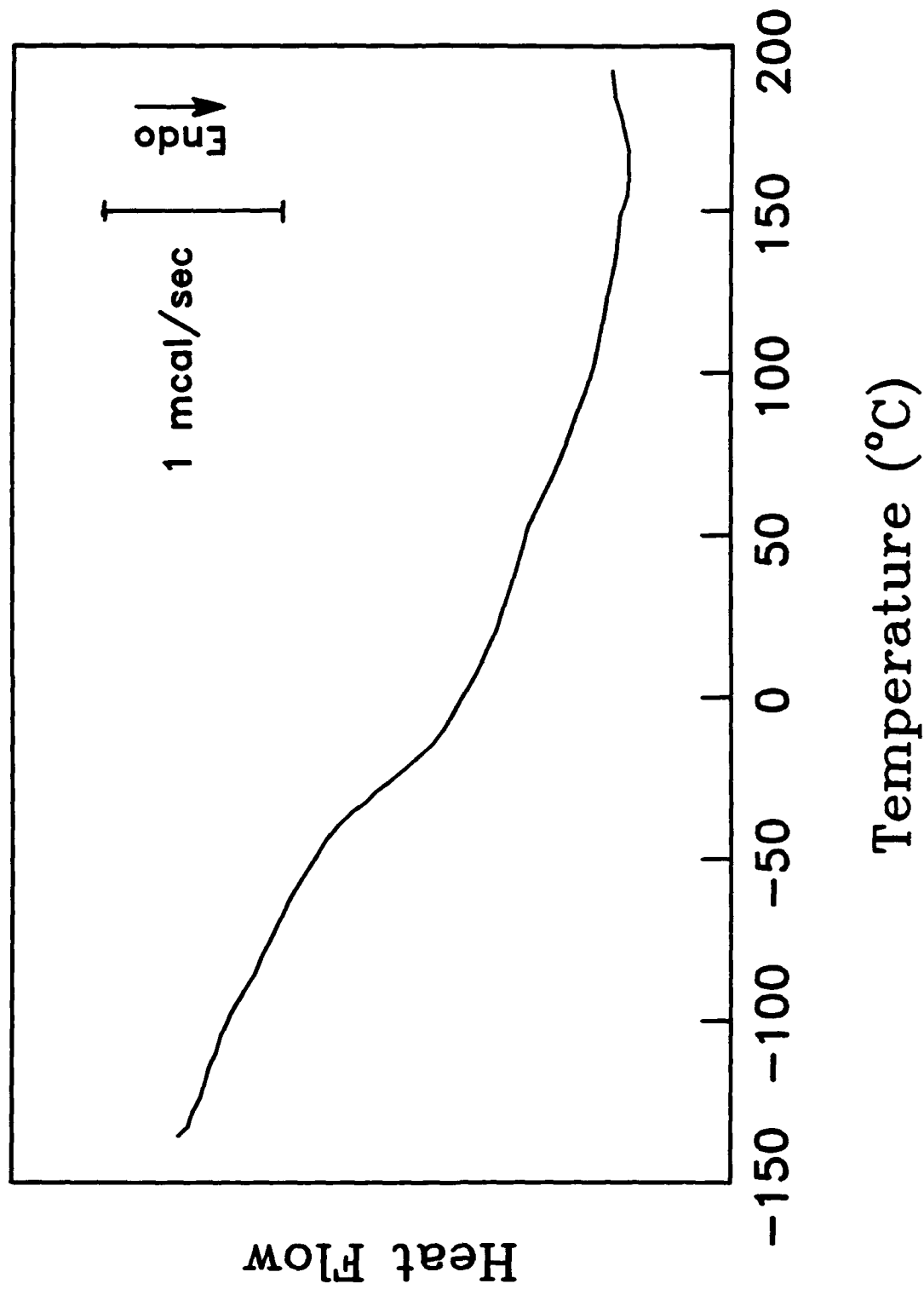
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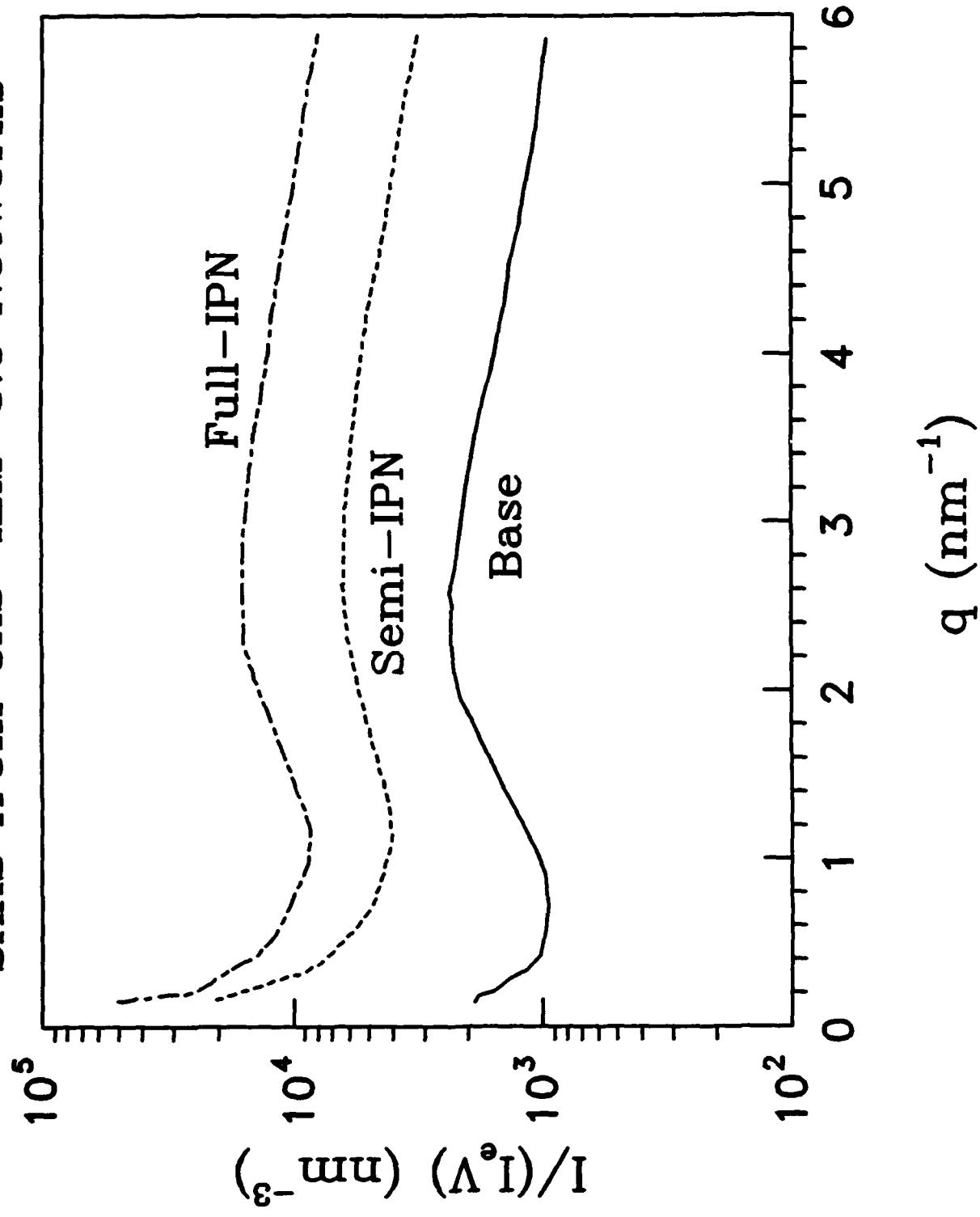
PMMA Full-IPNs



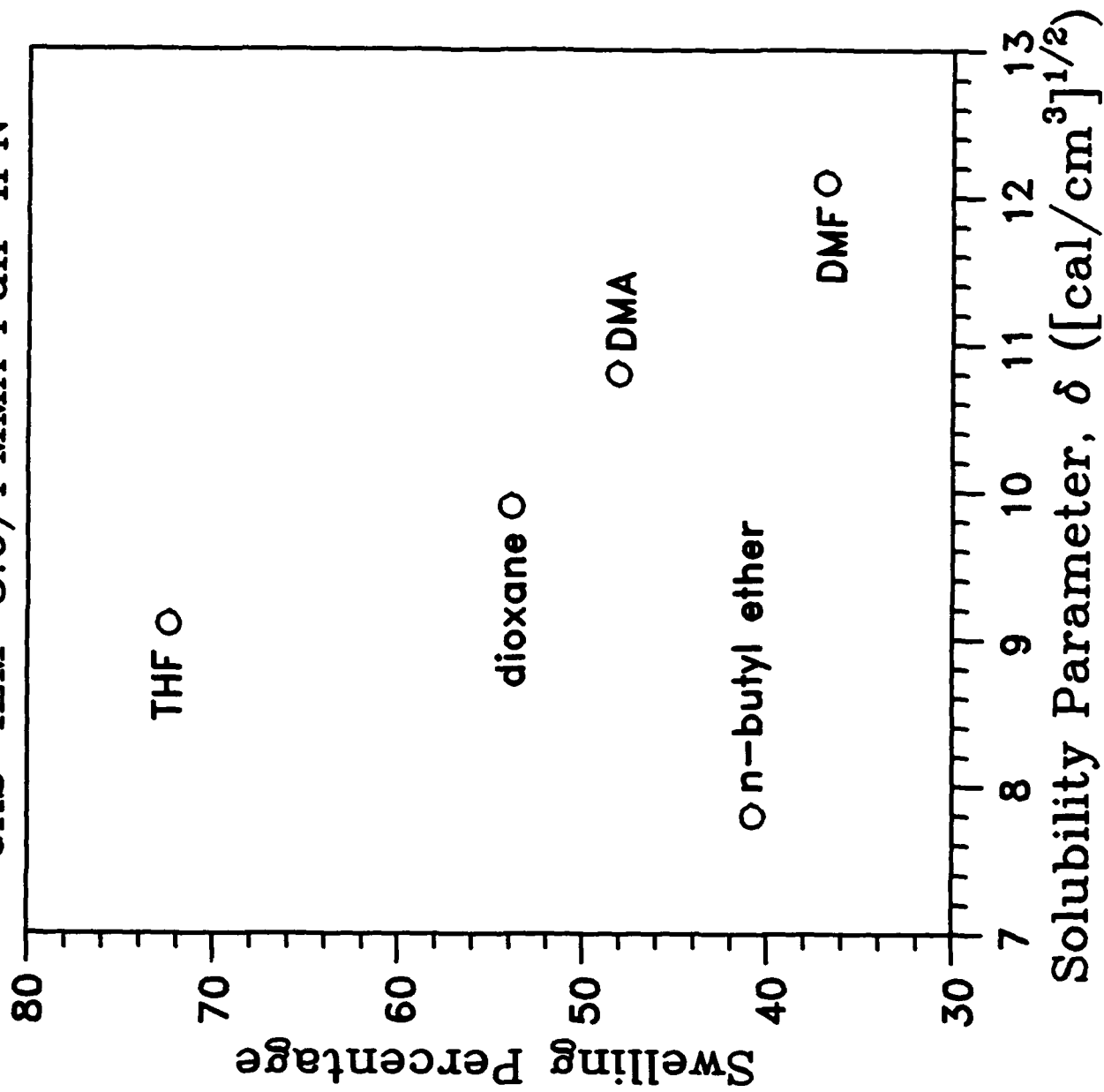
DSC from CAS-IEM-1.5/PMMA Full-IPN



SAXS from CAS-IEM-3.0 Networks



CAS-IEM-3.0/PMMA Full-IPN



Network Swelling in Dioxane

