3.1 Introduction

Photopolymers were first introduced as holographic recording material by Close et al. in 1969 [1]. Vinyl monomers, such as acrylate and methacrylate are used in most photopolymer systems.
Acrylamide based poly (vinyl alcohol) films constitute a low cost organic material, and a great deal of attention has been given to the composition of this photopolymeric system initiated by triethanolamine and methylene blue in recent years [2-8]. Blaya et al. reported a DE of nearly 80% in PVA/acrylamide system initiated with methylene blue and triethanolamine with 40 mJ/cm². But they prepared films using scientific thin layer chromatographic plate coater and also concentration of each component kept different [9]. In the present work, methylene blue sensitized acrylamide photopolymer system was used. Here films were prepared by gravity settling method. Optimization of each component is found to contribute to the holographic performance of the film [10].

Previously our research group has successfully recorded holographic gratings in acrylamide incorporated poly (vinyl alcohol) film, prepared by gravity settling method, with diffraction efficiency more than 70% with exposure energy of 120 mJ/cm², having a dye concentration of 2.09x10⁻⁴M. But on storage, DE was reduced to 10% within 6 days after recording [11]. The reason for the decrease may be due to the diffusion of residual dye molecules from destructive region to constructive region and by the instability of leuco form of the dye molecule [8]. Photopolymers are WORM materials and therefore the recorded gratings should be stable in these systems. In this chapter, studies were done to stabilize the recorded gratings by reducing the dye concentration.
3.2 Experimental
Film Preparation

All the materials used in this work were analar grade and were used without further purification. Photopolymer solution was prepared by dissolving 10 g Poly (vinyl alcohol), in 100 ml cold distilled water. (Molecular weight; 1, 25,000 and degree of hydrolysis, 86-90%). To this, acrylamide (AAm), Triethanolamine (TEA) and methylene blue (MB) were added and the solution was stirred well to get a homogeneous solution. The polymer film was prepared by gravity settling method under normal laboratory conditions (Relative Humidity-55-65%, temperature-30±2°C) and 48 hours of drying was required. The concentration of each component is given in Table 3.1.

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA</td>
<td>10% by weight</td>
</tr>
<tr>
<td>Acrylamide</td>
<td>0.25 – 0.5 M</td>
</tr>
<tr>
<td>Triethanolamine</td>
<td>0.01 – 0.1 M</td>
</tr>
<tr>
<td>Methylene blue</td>
<td>2.09x10^{-4}M - 0.7 x 10^{-5}M</td>
</tr>
</tbody>
</table>

3.3 Characterization

Tensile properties of the samples were measured using UTM-Shimadzu autograph AG-1 series and T<sub>g</sub> was measured using TA DSC-Q-100 instrument at a heating rate of 2°C/minute from 30°C-150°C under nitrogen atmosphere.
The optical characterization was done using Jasco V-570 spectrophotometer and modulation in refractive index was calculated using Kogelnik’s coupled wave theory. Optimization of various components was done by recording plane wave gratings on the film, using He-Ne laser (632.8 nm) by standard double beam method (chapter 2) and the gratings were reconstructed by 1µW He-Ne laser. Variation in spatial frequency, optimization of beam ratio, storage life and shelf life of the material were also measured.

3.4 Tensile Studies

For studying the effect of each component in the tensile properties of PVA, studies were done on pure PVA and PVA containing other additives. For this, samples were prepared and cut into rectangular pieces as explained in chapter 2.
From (fig.3.1), it is clear that no change in tensile strength was observed by the addition of TEA and doping with methylene blue (tensile strength of PVA- 26 N/mm², PVA+TEA -27 N/mm² and MB/PVA/AAm film-26 N/mm²).

But a change was observed in the case of elongation at break of the sample. From (fig.3.2), it can be seen that addition of TEA enhanced the % elongation at break of PVA from 365 to 434. Addition of electron donor cause an increase in DE as reported by B.M. John et al. [12] and enhancement in elongation at break of PVA support the above statement. Here TEA acts as a plasticizer and increases the chain flexibility and inturn enhances the elongation at break of PVA. During hologram recording, it appears that polymerization of monomer starts and proceeds rapidly in regions exposed to bright interference fringes. As conversion of monomers to
polymer occurs, fresh monomer diffuses in from neighboring dark regions, thus setting up concentration and density gradients that result in refractive index modulation [8]. If the chain flexibility is increased by the addition of TEA, this increases the diffusion of monomers and refractive index (RI) modulation. As diffraction efficiency (DE) depends on RI modulation, this will also get increased upon the addition of TEA.

### 3.5 DSC studies

From tensile studies it was clear that only TEA influences the mechanical properties of the polymer binder and therefore DSC studies were carried out with pure PVA and PVA containing the co-initiator TEA. Fig. 3.3, gives the DSC thermogram of these two.

![DSC curve of Pure PVA and PVA+TEA](image.png)

**Fig. 3.3. DSC curve of Pure PVA and PVA+TEA**
The glass transition temperature ($T_g$) of PVA is 86°C and addition of TEA has decreased the $T_g$ to 83°C. This is due to the plasticizing action of TEA on PVA matrix. Plasticizers are usually low molecular weight non-volatile substances, which when added to a polymer improves its flexibility, processibility and hence utility. As the lowering of $T_g$ of PVA occurs, the flexibility of polymer chain increases, then diffusion become easier and diffraction efficiency of the recorded grating also increases.

3.6 Optimization of methylene blue concentration

The photoinitiator determines the zone of absorption and therefore the wavelength used to record gratings. MB has absorption maximum in the red region of spectrum. So, for optimizing the concentration of the dye, gratings were recorded using He-Ne laser (emission at 632.8 nm). Methylene blue concentration was varied (keeping the concentration of all other component’s constant; weight % of PVA- 10, concentration of acrylamide -0.38 M, concentration of TEA- 0.05M) from $2.09 \times 10^{-4}$ M to $0.7 \times 10^{-5}$ M and samples were named as C 20, C14,...C 0.07 in (fig.3.4). Gratings were recorded at different exposure energies from 5 mJ/cm$^2$ to 130 mJ/cm$^2$ by keeping the recording angle 40° (our research group previously optimized the recording angle as 40° and further optimization in this material was done later) and power at the recording position as 4mW. From the figure, it can be seen that, for all the dye concentrations with the increase in exposure energy, RI modulation increases and resulted in increased DE, reaching a maximum and then decreases. At high
exposure, decrease in DE might be caused by cross-talk of holograms [13]. For C 20, maximum DE of 70% was obtained at exposure energy 120 mJ/cm² and for C14, the optimized exposure energy was 100 mJ/cm². For C 11, C 0.14 and C 0.07, the optimized exposure energy was 100 mJ/cm², 80 mJ/cm² and 50 mJ/cm² respectively. It is not possible to reduce or increase the concentration of dye beyond a limit; because if the concentration is very low, photopolymerization will be inefficient and if concentration is very high, the dye near the surface will act as a filter for the dye beneath it. Thus, unless the initiator fades to a non absorbing material during irradiation, only the monomer near the surface will be polymerized [14]. A maximum DE of 75% with exposure energy of 80mJ/cm² was obtained for the sample named as C 0.14 (dye concentration: 1.4×10⁻⁵M) (fig. 3.4). For this, a DE of 62% obtained at 5 mJ/cm² itself.

Fig. 3.4. Optimization of concentration of methylene blue
3.7 Optimization of concentration of acrylamide

For optimizing the concentration of acrylamide, MBPVA/AAm films were prepared by keeping the concentrations of methylene blue and triethanolamine constant. Acrylamide concentration was varied from 0.25 M to 0.5 M and the films were named as aa1, aa2... aa7. When the material was illuminated with He-Ne laser at a spatial frequency of 1080 lines/mm, photoreduction reaction occurred, yielding radicals that initiate radical polymerization reaction. When the concentration of acrylamide was increased, the energetic exposure necessary to obtain maximum DE was decreased, i.e., sensitivity increased. But it is not possible to increase the concentration of acrylamide indefinitely because the compatibility and solubility of this monomer in PVA is limited [9]. The maximum DE achieved remained approximately constant at high concentration of acrylamide, (fig.3.5).
Here for film aa7, this is the highest concentration, we have obtained a maximum DE of 68% at 30 mJ/cm$^2$, but DE obtained for all other samples remained nearly the same and a maximum DE of 75% was obtained for film aa5 (0.38 M) with exposure energy 80 mJ/cm$^2$. This was selected as the optimum concentration

### 3.8 Optimization of triethanolamine concentration

In order to optimize the concentration of triethanolamine, films were prepared by keeping the concentration of acrylamide and methylene blue constant. Concentration of triethanolamine was varied from 0.01 M to 0.1 M. During exposure, the incident light in a photoreduction reaction progressively converts the dye molecules into leuco methylene blue. As a result of this transformation, radicals capable of initiating photopolymerization reaction are generated [9]. Fig.3.6 shows concentration of TEA Vs % DE at 80 mJ/cm$^2$ with 1080 lines/mm. As the concentration of TEA increased, DE also increased, reaching a maximum and then decreased. Here maximum DE of 75% was obtained for 0.05 M. Amine acts as plasticizer that smoothen the network, favouring the solution and stability of the other components in the matrix and consequently the performance of the material [15]. After achieving a certain concentration, when the concentration of amine increased further, the primary free radical formation rate increased and the polymerization will also get speeded up. But the excess concentration will lead to cage effect, making the combination of free radicals terminated easily thus causing a reduction in diffraction efficiency [16].
So the optimized film is having concentration of methylene blue: $1.4 \times 10^{-5}$ M, acrylamide: 0.38 M, triethanolamine: 0.05 M. Further studies were done on this optimized sample.

### 3.9 Optical absorption studies

The film was exposed to an energy density of 80 mJ/cm$^2$ and the absorption spectra of the exposed and unexposed regions were taken. Fig. 3.7 shows a peak around 660 nm which is characteristic of methylene blue. But on exposure, the intensity of the peak decreased showing that bleaching occurred during irradiation.
3.10 Thickness measurement and calculation of RI modulation of the optimized film

The thickness of the dried film was measured using Dektak 6m Stylus profiler and a thickness of 130µm was obtained in the central part of the film.

The modulation in refractive index of the optimized sample before and after exposure was calculated using Kogelnik coupled wave theory:

\[ \Delta n = \sin^{-1} \left( \eta^{1/2} \right) \times \frac{\lambda \cos \theta}{\pi \times d}, \]

where \( \Delta n \) – RI modulation, \( \eta \) - DE, \( \lambda \) - wavelength of reading beam, \( \theta \) - angle inside the material measured from the normal to the surface and \( d \) – thickness of the film.

Using this equation a RI modulation of 1.52 x 10^{-3} was obtained.
3.11 Resolution of the optimized film

To find out the resolution of the material, gratings were recorded on the optimized sample at different inter-beam angles by keeping the exposure energy as 80 mJ/cm². Spatial frequency of each grating was determined using Bragg’s equation. Fig.3.8 is the plot of variation of DE with spatial frequency. Inter-beam angle was varied from 30°-80° and the corresponding spatial frequency was 818-2032 lines/mm. The efficiency was slightly increased with increase in spatial frequency, reaching a maximum of 75% at 1080 lines/mm and then decreased.

When the spatial frequency reached to 2032 lines/mm, diffraction efficiency reduced to 65%. The reduction in DE with spatial frequency could be due to migration of polymer chains, which have been initiated inside a bright region but grow into an adjoining dark
region. This would lead to averaging of the recorded refractive index profile. Such an effect would produce a weaker refractive index modulation and correspondingly lower DE at higher spatial frequencies [17].

### 3.12 Optimization of beam ratio

In order to study the effect of beam ratio on the diffraction efficiency of the recorded gratings, the intensity ratios of the two beams were varied by placing spatial frequency filters in the path of one beam. Gratings were recorded on the optimized film at exposure energy of 80 mJ/cm² and spatial frequency of 1080 lines/mm. The DE for different beam ratio is plotted (fig.3.9). A maximum diffraction efficiency of 75% could be achieved for beam ratio of 1: 1.

![Fig. 3.9. Variation of DE with beam ratio](image)
3.13 Storage life of the grating

Photopolymer films are WORM materials and therefore, storage life has great importance. To study the material storage life, kept at room temperature, gratings were recorded on the optimized sample at exposure energy of 80 mJ/cm² with spatial frequency 1080 lines/mm and diffraction efficiency was measured on successive days. The variation in DE with time is plotted (fig.3.10). Initially the material had a diffraction efficiency of 75% and after 2 months, it remained as 73% and after 5 months, the efficiency was 67% and after one year it was 43%. After this also, a decrease could be observed and after 3 years of recording, gratings could be read with low DE of 2 %.

![Graph showing the DE of MBPVA/AAm film on storage](image)

**Fig. 3.10. The DE of MBPVA/AAm film on storage**

The reason for decrease in the diffraction efficiency may be due to the diffusion of dye molecules from destructive region to
constructive region [8]. But in the present case, the concentration of dye molecule was very low and no more dye molecules may remain in the destructive region and storage life of MBPVA/AAm film could be improved by reducing the dye concentration.

3.14 Shelf life of the material

Shelf life of the material was studied by recording gratings on the optimized film at different time intervals after drying the sample. In all cases, gratings were recorded with an energy sensitivity of 80mJ/cm² with spatial frequency 1080 lines/mm. Fig.3.11 is the plot of decrease in DE on ageing of the film.

Grating with DE of 60% could be achieved up to two weeks and DE was decreased to 52% after one month. After 2 months, DE further reduced to 30 % and after 3 months, gratings could be recorded on this
sample with low diffraction of ~ 1 % DE and after 100 days, no gratings could be recorded.

In the case of commercially available Polygramma, which is in solution form, has a shelf life less than 6 months when the solution was kept below 20°C [18]. So inorder to improve the shelf life, the photopolymer mixture was kept in the solution form and stored at a temperature of 5°C ±3°C and a relative humidity of 30-50%. DE was monitored in each month by preparing the film and gratings were recorded as before. In this case, the same diffraction efficiency of 75% could be achieved after five months of solution preparation (fig.3.12).

Fig. 3.12. Improved shelf life of the optimized photopolymer solution

From the figure, it is clear that, by keeping the polymer mixture in solution form under controlled conditions, shelf life of the material could be improved.
3.15 Effect of UV Exposure on the storage life

Photopolymers usually subjected to post UV irradiation for stabilizing the gratings and upon UV exposure, the remaining dye molecules get reduced and the acrylamide monomers get polymerized and therefore no more diffusion occurs between the dark and bright regions and will get a stable DE. In order to study the effect of UV exposure on the storage stability of gratings, the recorded gratings were illuminated with a UV lamp for different times. When the films were exposed for more than 300 seconds, DE obtained was very low (therefore the results not included here). At high exposure, the decrease in DE is due to crosslinking of PVA chain [19]. A DE of 75% was obtained without UV exposure and the (fig.3.13) shows the variation in DE with UV exposure.

![Fig. 3.13. Optimization of UV exposure time](image-url)
DE of the grating exposed for 5 seconds, 10 seconds and 15 seconds was reduced to 55% and for the grating exposed for 30 seconds; DE was decreased to nearly 60%. After this, an increase in DE was observed and a maximum DE of 77% was obtained when exposed for 180 seconds and after this, a reduction in DE could be observed. Depending on the PVA chain length, dye concentration and UV exposure, the optical recording efficiency was improved, diminished, or had no change [19].

For studying the storage life of the grating upon UV exposure, DE of the gratings was monitored at different time intervals and the values of DE on storage are plotted (fig.3.14).

![Fig. 3.14. Effect of UV exposure on storage](image)
Chapter - 3

From the figure, it is clear that upon UV exposure, DE increased from 75% to 77% and it remained as such for months. A reduction in DE was observed only after 7 months and it reduced to 75%; in 10 months, a DE of 73% could be achieved and gratings could be read with a DE of 65% within one year of recording and after one year, DE was reduced to 63%.

In order to confirm the absence of crosslinking, the tensile strength of the exposed PVA films were compared with that of unexposed film and shows in (fig.3.15). From this it is clear that there was no crosslinking in PVA as crosslinking is expected to improve tensile strength.

Fig. 3.15. Comparison of tensile strength of UV exposed films with unexposed film

The comparison of the storage life of MBPVA/AAm film with and without UV exposure is given in table 3.2
Table 3.2. Comparison of storage life of grating with and without UV exposure

<table>
<thead>
<tr>
<th>Material</th>
<th>Storage life (one year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBPVA/AAm film without UV exposure</td>
<td>43%</td>
</tr>
<tr>
<td>MBPVA/AAm film after UV exposure</td>
<td>63%</td>
</tr>
</tbody>
</table>

From the table, it is clear that UV exposure has improved the storage life of the material.

3.16 Protection of the film

Optical disk media must be protected from physical and environmental damage and from particulate contamination. Favoured protective schemes include encapsulation and air-sandwich structures. Both systems are designed to keep dust particles away from the plane of focus at the recording surface, thereby reducing impact on signal quality. Encapsulation is achieved by solvent coating a polymer film over the recording layer. In the air-sandwich structure, which consists of two disks bonded face to face and separated by a spacer-defined air gap, the substrate becomes the protective layer [20].

The use of sealing techniques to improve the properties of holographic materials are common. Materials such as dichromated gelatin must be sealed from the environment to prevent water absorption destroying the gratings. Silver halide films typically have an inert outer layer at their surface, referred to as an anti-stress layer. In 1997, Ketai et al. reported the use of PMMA as a sealant, the holographic recording material in this case being methylene blue-sensitized dichromated gelatin.
DuPont Omnidex HRF-700X001-20 material is supplied sandwiched between two A5 sized sheets of Mylar and stored in a light-proof wrapping [21].

In the present case, recording layer was sealed using air-sandwiched and encapsulated structures. Epoxy sealant and cyanoacrylate sealant were used as air-sandwiched structures and PMMA sealant was used as encapsulated structure and their effect on storage and shelf life of the recorded gratings were studied.

3.16.1 Effect of epoxy sealant on the storage life and shelf life of gratings

Preparation of epoxy sealant was given in chapter 2 and this was applied on the sides of a clean glass plate placed over the recording layer. The sealant was applied before and after recording the grating and the DE was almost the same in both the cases (DE-67%). The DE on storage was monitored and plotted (fig.3.16). After 3 months of recording, DE was 62%, after 6 months, 58% and one year 47%. In the case of unsealed film, in the initial stages of storage, a higher DE was obtained compared to the sealed films but after one year of recording, the DE was the same as that of sealed films. But after 3 year, gratings could be read with a DE of 12% (unsealed film, it was only 2%). From this it is clear that, the rate of reduction in DE was low in sealed films compared to the unsealed films and by using epoxy sealant, the storage life of the film could be slightly improved.
Fig. 3.16. Comparison of DE on storage of MBPVA/AAm film with epoxy sealant

For studying the shelf life of the film, gratings were recorded using the optimized parameters for different times after drying the film and the change in DE with time is plotted (fig.3.17). Upto one month, a DE of 60% could be obtained, within 2 months, DE reduced to 35% and in 3 months, it was nearly 20%. Again a reduction could be observed and gratings could be recorded with low DE in the 4th month after drying the films (in the case of unsealed films, no gratings could be recorded after 3 and half months, section 3.14). So shelf life of the film could be improved by using epoxy sealant.
3.16.2 Studies on the storage life and shelf life of MBPVA/Am films with cyanoacrylate sealant

The acrylate sealant was applied as done in the case of epoxy sealant, before and after recording the gratings and the DE obtained was almost similar in both the cases (nearly 60%) and DE on storage was studied and plotted (fig.3.18). The DE was not stable and reduced to 56% within one month after recording and after two months, DE was reduced to 53% and then to 45% after 3 months.
Fig. 3.18. DE on storage of cyanoacrylate sealed MBPVA/AAm films

For studying the shelf life of the sealed film, gratings were recorded and the variation in DE with ageing of the film is plotted (fig.3.19).

Fig. 3.19. DE on ageing of cyanoacrylate sealed MBPVA/AAm films
It can be seen that DE of 60% was obtained only for a few days after drying and after one month, DE of 56% was obtained and after 2 months, DE of 50% could be obtained. After 3 months of film preparation, gratings could be recorded with 40% DE. It can be seen that, by using cyanoacrylate sealant, the shelf life of the film could be slightly improved compared to epoxy sealed film.

3.16.3 Effect of PMMA sealing on the storage life and shelf life of the MBPVA/AAm films

When epoxy sealant or cyanoacrylate sealant were used, the film could be sandwiched between two glass slides and also there was no significant improvement in material’s properties, PMMA was used as sealant and in this case no sandwiching of the film was needed but the films were dipped in PMMA solution and kept for drying. Here different concentrations of PMMA solutions were prepared (1% -5%). For optimizing PMMA concentration, films were dipped in these solutions before and after recording of grating for one to three times. But only for the film dipped in 1% PMMA solution had better film quality. Therefore studies were done on these films only and better results were obtained when gratings were recorded, after dipping the film in 1% PMMA solution for two times.

In order to find the storage life of the sealed film, DE of the recorded gratings were monitored at different time intervals and plotted (fig.3.20). From the figure, it is clear that, there was no reduction in the initial DE compared to sandwiched sealants and a DE of 69% could be achieved after 6 months also, (in the case of
epoxy sealed films, a DE of 58% could be obtained after 6 months, section 3.16.1).

![Graph showing DE on storage of PMMA sealed MBPVA/AAm films](image)

**Fig. 3.20. DE on storage of PMMA sealed MBPVA/AAm films**

For studying the shelf life of the film, the films were dipped twice in 1% PMMA solution and kept for drying. Gratings were recorded on the films on ageing of the film and DE with ageing is plotted (fig.3.21). From the graph, it is clear that gratings could be recorded with a DE of 70% even after 3 months of preparation (for epoxy and acrylate sealed film, DE of 20% and 40% respectively could be obtained after 3 months, section 3.16.1 and 3.16.2). So the results showed that PMMA sealed films had better DE on storage and ageing compared to epoxy and acrylate sealants.
Comparison of the results of unsealed and sealed film is given in table 3.3.

**Table 3.3. Comparison of storage life and shelf life of the material with and without sealant**

<table>
<thead>
<tr>
<th>Material</th>
<th>Storage life (3months)</th>
<th>Shelf life (3months)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsealed MBPVA/AAm film</td>
<td>67%</td>
<td>1%</td>
</tr>
<tr>
<td>Epoxy sealed film</td>
<td>62%</td>
<td>20%</td>
</tr>
<tr>
<td>cyanoacrylate sealed film</td>
<td>52%</td>
<td>40%</td>
</tr>
<tr>
<td>PMMA sealed film</td>
<td>70%</td>
<td>70%</td>
</tr>
</tbody>
</table>

So PMMA sealed films had better storage life and shelf life and it could be used for sealing the films more easily.
3.17 Conclusion

Methylene blue sensitized PVA/AAm films were fabricated; but possessed poor storage life and by reducing the concentration of the dye, storage life of the material could be improved. The shelf life of the material could be improved by keeping the photopolymer mixture in solution form under controlled temperature. Upon exposure to UV light for 180 seconds, the storage life of the material could be further improved. For protecting the films from external dust and contaminants, sealants were used and the storage life and shelf life of the material could be improved by sealing; out of which, PMMA sealed films showed better results.

References


[18]. http://www.polygramma.com


......FOGR......
### CORRECTIONS

**Sec.3.4 & 3.5**

It is concluded that TEA acts as a plasticizer and therefore, it increases the elongation at break of PVA from 365% to 434% and decreases the glass transition temperature from 86 to 83°C. However, the tensile strength is not affected by the plasticization. The reason for this unexpected trend may be given.

The MB/PVA/AAm film has given tensile strength identical to PVA (Fig.3.1), despite the incorporation of a fairly large quantity of acrylamide in the film (1.8 g to 3.8). This also needs explanation.

The addition of TEA has increased the elongation at break (%) of PVA due to the plasticization effect. Triethanolamine may be occupying positions in between the polymer chains. There can be some interaction between triethanolamine and PVA which can lead to a minor increase in tensile strength.

MB/PVA/AAm film contains acrylamide as the monomer, methylene blue as the sensitizer, triethanolamine as the initiator and PVA acts as a matrix to the components.

Methylene blue has absorption in the red region of the spectrum and after the absorption of light it changes to leuco form and leads to polymerization. Therefore there is a chance for the polymerization of the monomer during drying of the film under sunlight. This may lead to the formation of a semi interpenetration network with the same tensile strength.
Sec.3.5:fig.3.3

The DSC curves of all the 4 samples appear as a broad endothermic peaks starting from room temperature to approx.140°C. What is the phenomenon/transition corresponding to the broad DSC peaks? How was the Tg inferred from the peaks?

DSC studies were done on different samples and the glass transition temperature was determined by taking the tangent.