

## Chapter 7

# Relaxation processes in poly(cyclohexyl methacrylate)

The relaxation processes occurring in glassy polymers, have many similarities with that of the molecular glasses formed by supercooling a monomeric liquid.<sup>1-3</sup> These processes designated as  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ - etc. in the decreasing order of temperature, are due to the various modes of molecular mobility within the bulk sample and are extremely important in the design aspect of the polymer for use in a particular range of temperature.<sup>4,5</sup> While the  $\alpha$ -process is a cooperative relaxation of large segments of the back-bone in a polymer (or many molecules in a monomeric liquid); the sub- $T_g$  (i.e.  $\beta$ -, and  $\gamma$ -) processes are always characterized by an excitation over a localized potential barrier (and hence is non-cooperative in nature). While, in a polymeric glass the  $\beta$ -process is caused by a localized motion of about three to four carbon atoms, in the case of a monomeric glass it is not very clear whether it is inter or intra- molecular in nature, (although some researchers believe it to be of dominantly intra-molecular in nature<sup>2</sup>). In glass physics, it is strongly believed that the occurrence of the  $\beta$ -process is a characteristic feature of the glass transition phenomena in general. A lot of experiments have been designed in the recent years to show that the  $\beta$ -process indeed exists in all glasses formed by supercooling of a liquid.<sup>6-9</sup> Therefore, it is of interest to see whether it is so even with glassy polymers.

In the case of polymers, the occurrence of  $\beta$ -process due to a localized movement of

smaller segment of polymer is a very well known phenomena. Typical is the example of poly(vinyl chloride) which has no side group, but still exhibits a strong  $\beta$ -process.<sup>4,5</sup> Many other such examples can be found in the above references. However, polymers which have bulky side groups, have a tendency of not revealing such a process; obviously because of the steric hindrance for mobility of such monomeric units (with bulky side groups) is expected to be very high. Two polymers namely, poly(vinyl acetate) (PVA) and poly(cyclohexyl methacrylate) (PCHMA) belong to this group of polymers. A careful examination of the data of PVA clearly reveals the existence of a  $\beta$ -process<sup>10</sup> and therefore, it is of interest to see whether we can find a similar process in PCHMA.

Relaxation processes in PCHMA has been the subject of discussion in a number of research articles. Ishida<sup>4,5</sup> and Heijboer<sup>11,12</sup> reported three relaxation processes in PCHMA, namely  $\alpha$ ,  $\beta$ ,  $\gamma$  in order of decreasing temperature with dielectric and mechanical means. Ribes *et al.*<sup>13</sup> reported yet another process in the low temperature  $\delta$ -process while reporting that the  $\beta$ -relaxation is strongly hindered. The photon correlation spectroscopic (PCS) results reported by Fytas *et al.* (Ref. 14,15) also do not show any  $\beta$ -relaxation in the sub- $T_g$  region. In view of the above discussion, a necessity has been felt to critically study the various relaxations in PCHMA using a wide frequency relaxation technique. In this context, we critically studied PCHMA using dielectric spectroscopy.

## 7.1 EXPERIMENT

The sample Poly(cyclohexyl methacrylate) or PCHMA was obtained from Aldrich Co., USA in powdered form. The average molecular weight reported was 65,000 and the corresponding  $T_g$  was reported in the Aldrich catalogue, to be 377 K. The sample was used without any further purification. For the dielectric measurements the frequency range 20 Hz- 1 MHz, an HP 4284A precision LCR meter is used. For frequencies below 20 Hz- $10^{-3}$  Hz, a Keithley Model No. 617 Programmable Electrometer in combination

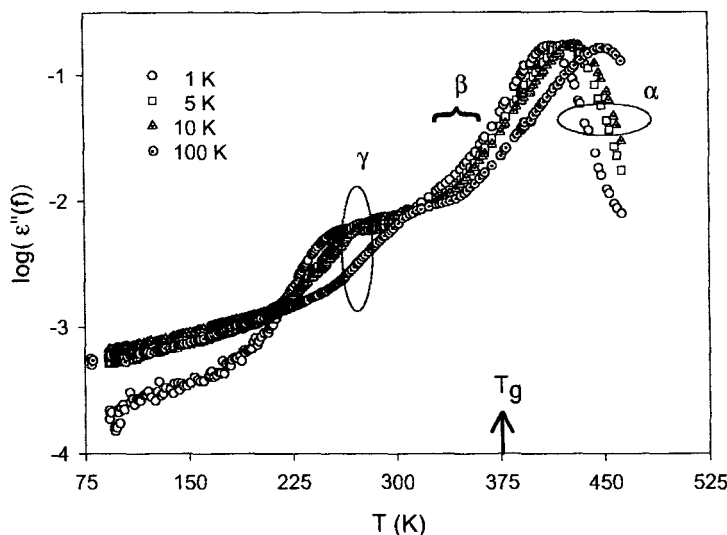


Figure 7.1: Variation of  $\epsilon''$  with temperature at different test frequencies in PCHMA.

with a digital storage oscilloscope (DSO) DSO-2200 has been used. Both solid and liquid dielectric cells have been used for the dielectric study. We have filled the sample in the liquid cell with an empty capacitance of about 40 pF at a temperature much above  $T_g$  and corrected the cell parameters  $C_0$  and  $C_l$  by comparing the data from the sample from the solid cell in the form of pellet by linear regression of the capacitance in the liquid cell  $C_p$  vs  $\epsilon'$  (the real part of the permittivity) in the solid cell at the same temperature for the range of frequencies 1 KHz-100 KHz. (Because of the poor DC conductivity of the sample, there is no contribution toward Maxwell-Wagner polarization during the course of our measurements).

## 7.2 RESULTS

To give the reader an idea of the various relaxation processes, we have plotted the temperature (T-) variation of dielectric loss at fixed frequencies in Figure 7.1. Apart from the very well resolved processes labeled as primary ( $\alpha$ -) and tertiary ( $\gamma$ -) relaxations as shown in the figure, one can see the secondary ( $\beta$ -) process as a shoulder on the lower temperature side of the  $\alpha$ - process. The spectral dependence of  $\alpha$ - process is shown in Figure 7.2(a) at different temperatures.

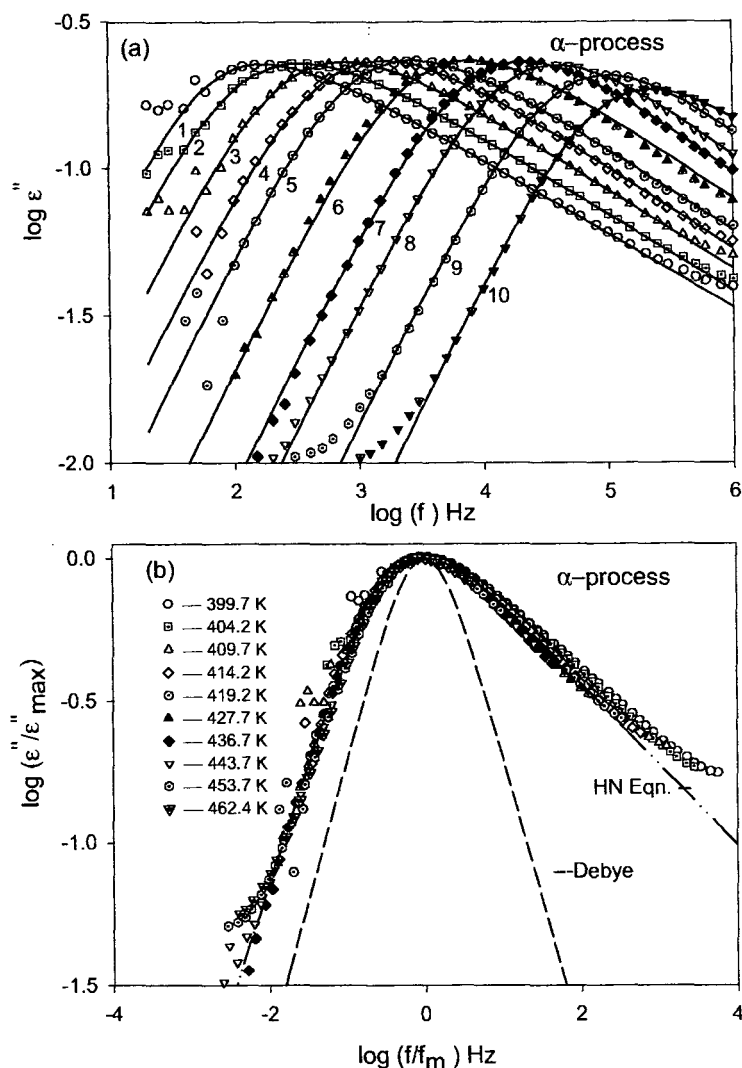


Figure 7.2: For  $\alpha$ - process at different temperatures in PCHMA. Dielectric loss ( $\epsilon''$ ) vs frequency ( $f$ ) curves labeled correspond to 1: 399.7 K; 2: 404.2 K; 3: 409.7 K; 4: 414.2 K; 5: 419.2 K; 6: 427.7 K; 7: 436.7 K; 8: 443.7 K; 9: 453.7 K; 10: 462.4 K respectively. The thick lines refer to the best fit to Eq. (1.41). (b): Dielectric loss ( $\epsilon''$ ) normalized to its peak loss value ( $\epsilon''_{max}$ ) vs frequency ( $f$ ) normalized to its peak loss value  $f_m$ . Also shown in the figure is the Debye behavior (dashed line) and HN fits to the parameter values ( $\alpha = 0.152, \beta = 0.341, f_0 = 2.65 \times 10^3, \Delta\epsilon = 1.0092$ ).

We have analyzed the relaxation data using the imaginary part of Havriliak-Negami (HN) shape function.<sup>16</sup> The corresponding least-square fits are shown in Figure 7.2(a) as thick lines to give an idea of goodness of the fits. The corresponding parameters are given in Table I. Also included in the Table I the peak loss frequency ( $f_m$ ) calculated from the parameters of Eq. (1.41) (see Ref. 17 for details on this topic). In Figure 7.2(b) we have shown the same data of Figure 7.2(a) plotted in a normalized form to give the reader some idea about the T-dependence of the shape of the spectra and its deviation from Debye behavior. Also given in Figure 7.2(b) is a fit to the HN equation for the

parameters given in the Figure caption of Figure 7.2(a). The corresponding values are  $\log f_0 = 12.3$ ,  $E = 73$  kJ/mol for the  $\beta$ - process;  $\log f_0 = 12.3$  and  $E = 45$  kJ/mol for the  $\gamma$ - process.

**Table I. Details of Relaxation-processes**

Process	Temp(K)	$\alpha_{HN}$	$\beta_{HN}$	$f_0(\text{Hz})$	$\log f_m(\text{Hz})$	$\Delta\epsilon$
$\alpha$	404.2	0.151	0.307	$1.04 \times 10^2$	2.537	1.0540
	414.2	0.164	0.333	$5.13 \times 10^2$	3.204	1.0400
	427.7	0.152	0.341	$2.65 \times 10^3$	3.898	1.0092
	443.7	0.157	0.388	$1.52 \times 10^4$	4.599	0.9062
	453.7	0.152	0.400	$4.03 \times 10^4$	5.007	0.7960
$\beta$	331.2	0.792	1.000	$6.37 \times 10^0$	0.804	0.2562
	346.7	0.768	1.000	$2.26 \times 10^1$	1.354	0.2982
	351.2	0.759	1.000	$3.18 \times 10^1$	1.503	0.3213
$\gamma$	254.4	0.493	1.000	$7.96 \times 10^2$	2.901	0.0330
	267.4	0.487	1.000	$2.27 \times 10^3$	3.357	0.0373
	274.4	0.525	1.000	$3.18 \times 10^3$	3.503	0.0423

The spectral dependence of  $\beta$ -relaxation of the dispersion is shown in Figure 7.3(a) at different temperatures. The corresponding parameters are given in the Table I. The high frequency tail on the  $\beta$ -process is because of the presence of  $\gamma$ -process whose  $f_m$  is located above 1 MHz of frequency in the same temperature region. In Figure 7.3(b), the data corresponding to the  $\gamma$ -relaxation process are shown. The parameter values of the fits are also given in Table I. The complete Arrhenius plot is given in Figure 7.4. The data of others are also given for the purpose of comparison. The  $\alpha$ -relaxation process clearly shows a non-Arrhenius temperature dependence and is found to follow the critical power law equation.<sup>1</sup> The parameters of the best fit to the Eq. (1.54) are  $\log f_0(\text{Hz}) = 9.71$ ,  $r = 10.96$  and  $T'_g = 330.0$  K. Alternately, the data can also be described equally well by the Vogel-Fulchers-Tammanns equation.<sup>13</sup> The parameters of the Eq. (1.53) for the  $\alpha$ -process are,  $\log f_0(\text{Hz}) = 11.48$  and  $B = 2730.3$  K and  $T_0 = 270.43$  K. The  $f_m$  values of both  $\beta$ - and  $\gamma$ - processes are analyzed using the Arrhenius equation.<sup>4,5</sup>

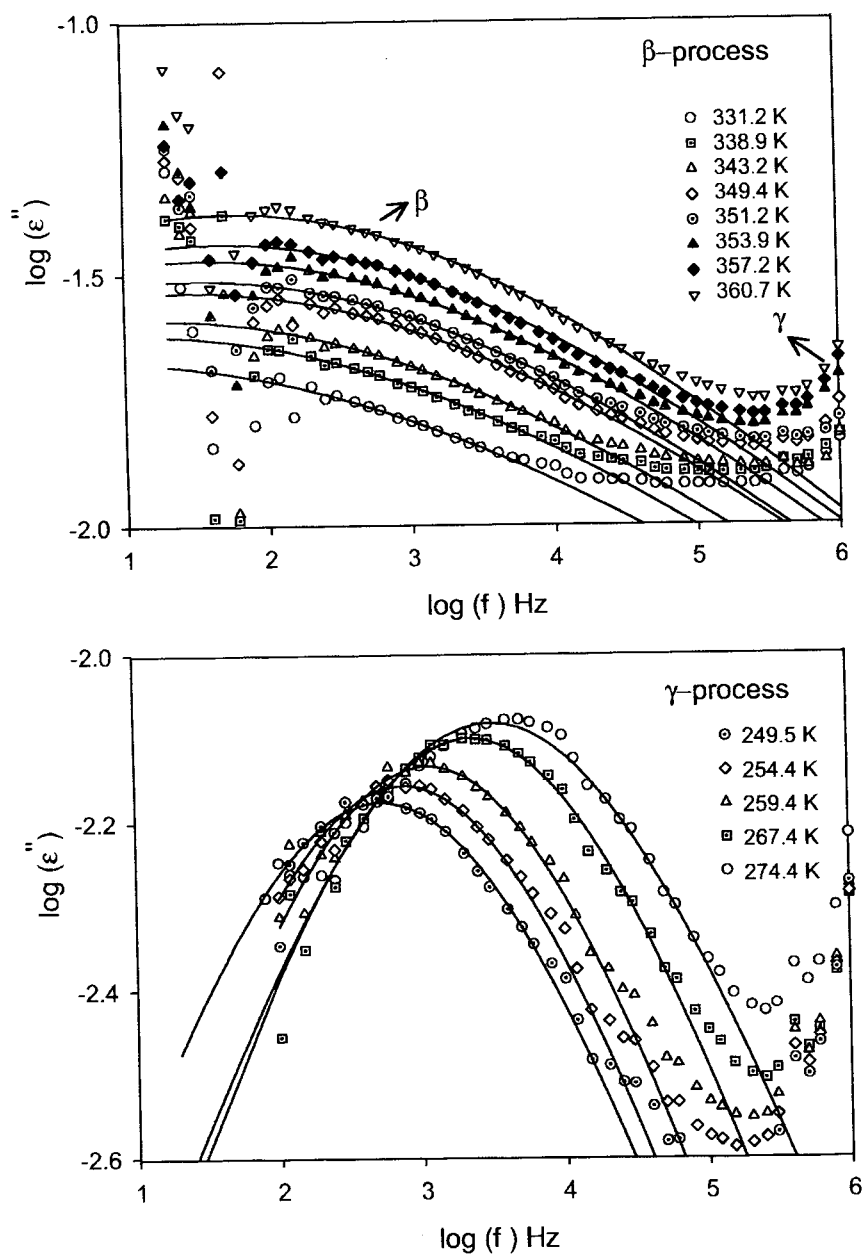


Figure 7.3: Dielectric loss ( $\epsilon''$ ) vs frequency ( $f$ ) at different temperatures in PCHMA: (a)  $\beta$ -process and (b)  $\gamma$ -process. Thick lines refer to the best fit to Eq. (1.41)

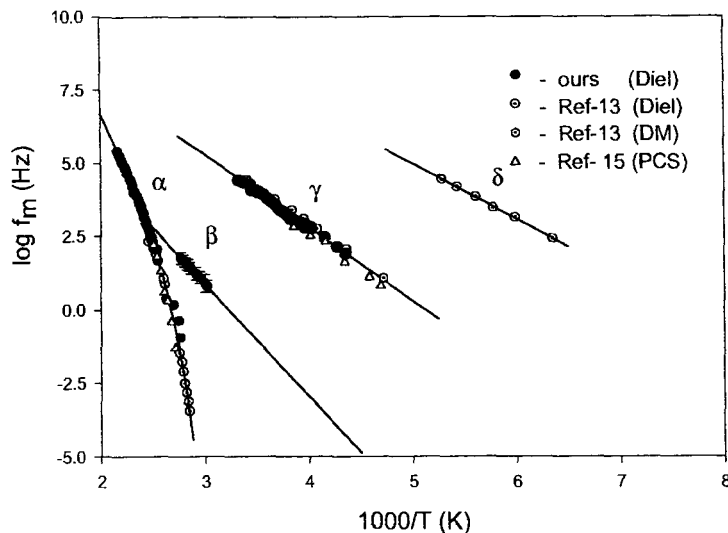


Figure 7.4: Complete Arrhenius diagram of PCHMA. The thick line on  $\alpha$ -process corresponds to the fit to the Eq. (1.41). (The parameters are  $\log f_0 = 9.71$ ,  $r = 10.96$ ,  $T_g = 330.0$  K). The data from other references are also given with different symbols which contain mechanical dynamical results of Heijboer (Ref. 11,12) dielectric results of Ishida (Ref. 4,5) and PCS data of Fytas (Ref. 14,15). The thick lines in case of  $\beta$ -,  $\gamma$ -,  $\delta$ - are the least square fits to the Eq. (1.37)

## 7.3 DISCUSSION

Following are the highlights of our study.

(i). The  $\alpha$ - process was earlier reported<sup>13</sup> to be of Cole-Davidson type, i.e.  $\alpha_{HN} = 0$  in Eq. (1.41), but our study clearly shows deviations from Cole-Davidson type of behaviour for the  $\alpha$ - process (see Figure 7.2 and Table I).

(ii) We have succeeded in seeing the  $\beta$ - process as a clearly distinct process [Figure 7.3(a)] and the corresponding activation energy is 73 kJ/mol, as is expected for the reorientation of two to three monomeric units with bulky side groups.<sup>4,5,10,11,12</sup>

(iii). The  $\gamma$ -process is very symmetrical in its spectral characteristic [Figure 7.3(b) and Table I] and the corresponding  $E$ -value is 45 kJ/mol which is slightly smaller than what was reported by Ribes *et al.*<sup>13</sup> It is in all probability, intra-molecular in nature as suggested earlier by others.<sup>11-13</sup>

(iv). We have not found any observable  $\delta$ - process as in the study of Heijboer,<sup>11,12</sup> although Ribes *et al.*<sup>13</sup> had reported it in their dielectric measurements.

## 7.4 CONCLUSIONS

We have succeeded in locating the  $\beta$ - process thought to be characteristic of all the glassy systems, which in all probability, it is due to the localized reorientational motion of two to three monomeric units of the polymer back-bone.

## 7.5 REFERENCES

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