CHAPTER II

EXPERIMENTAL DETAILS

II.1 Introduction

The double refraction of six liquid crystalline substances and their mixtures has been studied. The measurements were made On uniaxial oriented liquid crystalline layers, using the principle of minimum deviation. Such optically uniaxial layers could be obtained from the nematic states. The measurements of the principal refractive indices were carried out at various temperatures by using a spectrometer, at the monochromatic wavelength of a sodium source. The crystalline liquid was placed in the space between the two rectangular glass plates forming a small-angle prism. Because of a slight mechanical influence imposed by the bounding glass plates on the molecular arrangement within the nematic liquid crystal, the oriented layer behaves optically like a uniaxial crystal with the direction of the optic axis normal to the bounding surfaces.

II.1.1 Liquid crystal prism

Since the refractive indices of the liquid crystals can be calculated from the method of minimum deviation, we shall now briefly discuss the passage of light through a liquid crystal prism[1].

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[1] M.Born and E.Wolf, Principles of Optics, 4th Edition, Pergamon Press Ltd., London, (1970), p.177

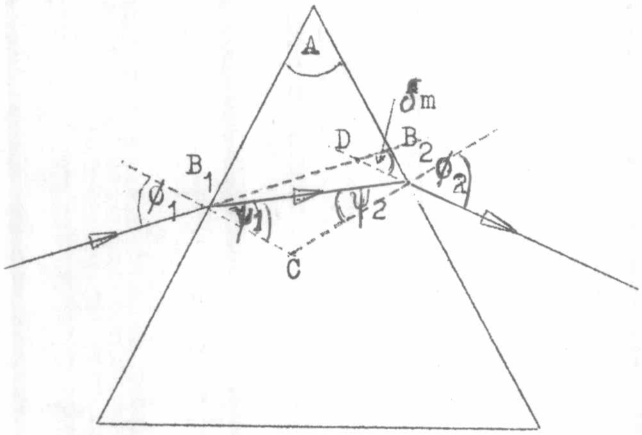


Fig. 3 Schematic diagram of passage of a ray through a liquid crystal prism.

Let A be the angle between the two faces of the prism. It is assumed that the edge in which the two faces meet is perpendicular to the plane which contains the incident, transmitted, and emergent rays as in Fig 3

Let B_1 and B_2 be the points of intersection of the incident and the emergent ray with the two faces, ϕ_1 and ψ_1 the angle of incidence and refraction at B_1, and ψ_2 and ϕ_2 the inner and outer angles at B_2 (i.e. the angles which the ray B_1B_2 and the emergent ray make with the normal at B_2). Further let C be the point of intersection of the normals to the prism at B_1 and B_2, and D the point of intersection of the incident and the emergent rays.

If δm is the angle of deviation, i.e. the angle which the emergent ray makes with the incident ray, then

$$\phi_1 + \phi_2 = \delta m + A \qquad \ldots\ldots\ldots\ldots\text{⑪}$$

$$\psi_1 + \psi_2 = A \qquad \ldots\ldots\ldots\ldots\text{②}$$

Further, by the law of refraction

$$\sin\phi_1 = n\sin\psi_1 \qquad \cdots\cdots\cdots\cdots \textcircled{3}$$

$$\sin\phi_2 = n\sin\psi_2 \qquad \cdots\cdots\cdots\cdots \textcircled{4}$$

where n is the refractive index of the liquid crystal with respect to the surrounding air. The deviation δm will have an extremum when

$$\frac{d\delta m}{d\phi_1} = 0 \qquad \cdots\cdots\cdots\cdots \textcircled{5}$$

Using ① this implies that

$$\left(\frac{d\phi_2}{d\phi_1}\right)_{\text{extr.}} = -1 \qquad \cdots\cdots\cdots\cdots \textcircled{6}$$

Now we have from ②, ③ and ④

$$\left.\begin{aligned} \frac{d\psi_1}{d\phi_1} &= -\frac{d\psi_2}{d\phi_1} \\ \cos\phi_1 &= n\cos\psi_1\frac{d\psi_1}{d\phi_1} \\ \cos\phi_2\,\frac{d\phi_2}{d\phi_1} &= n\cos\psi_2\frac{d\psi_2}{d\phi_1} \end{aligned}\right\} \qquad \cdots\cdots\cdots\cdots \textcircled{7}$$

and hence, on elimination

$$\frac{d\phi_2}{d\phi_1} = -\frac{\cos\phi_1\cos\psi_2}{\cos\psi_1\cos\phi_2} \qquad \cdots\cdots\cdots\cdots \textcircled{8}$$

From ⑥ and ⑧ it follows that, for an extremum,

$$\frac{\cos\phi_1 \cos\psi_2}{\cos\psi_1 \cos\phi_2} = 1$$

.... ⑨

hence, on squaring and using ③ and ④,

$$\frac{1 - \sin^2\phi_1}{n^2 - \sin^2\phi_1} = \frac{1 - \sin^2\phi_2}{n^2 - \sin^2\phi_2}$$

.... ⑩

This equation is satisfied by

$$\left.\begin{aligned} \phi_1 &= \phi_2 \\ \text{then} \quad \psi_1 &= \psi_2 \end{aligned}\right\}$$

.... ⑪

To determine the nature of the extremum we must evaluate $\frac{d^2\delta_m}{d\phi_1^2}$. From ① and ⑧ ,

$$\frac{d^2\delta_m}{d\phi_1^2} = \frac{d^2\phi_2}{d\phi_1^2} = \frac{d\phi_2}{d\phi_1} \cdot \frac{d}{d\phi_1}\left[\log\left(\frac{d\phi_2}{d\phi_1}\right)\right]$$

$$= \frac{d\phi_2}{d\phi_1}\left[-\tan\phi_1 - \tan\psi_2\frac{d\psi_2}{d\phi_1} + \tan\psi_1\frac{d\psi_1}{d\phi_1} + \tan\phi_2\frac{d\phi_2}{d\phi_1}\right]$$

.... ⑫

When $\phi_1 = \phi_2$, $\psi_1 = \psi_2$ this becomes with the help of ⑥ , ⑦ ③ and ④

$$\left(\frac{d^2\delta_m}{d\phi_1^2}\right)_{\text{extr.}} = 2\tan\phi_1 - 2\tan\psi_1\frac{\cos\phi_1}{n\cos\psi_1}$$

$$= 2\tan\phi_1\left[1 - \frac{\tan^2\psi_1}{\tan^2\phi_1}\right]$$

.... ⑬

Since $n > 1$, $\phi_1 > \psi_1$; also since $0 < \phi_1 < \frac{\pi}{2}$, $\tan\phi_1 > 0$. Hence $(d^2\delta m/d\phi_1^2) > 0$, so that the deviation is a minimum. According to (11) it takes place when the passage of the rays through the prism is symmetrical. The minimum value of the deviation then is

$$\delta m_{min} = 2\phi_1 - A \qquad \text{............ (14)}$$

In terms of δm_{min} and A, the angle of incidence and the angle of refraction at the first face of the prism are

$$\phi_1 = \tfrac{1}{2}(\delta m_{min} + A) \; ; \; \psi_1 = \tfrac{1}{2}A \qquad \text{............ (15)}$$

so that

$$n = \frac{\sin\phi_1}{\sin\psi_1} = \frac{\sin\frac{1}{2}(\delta m_{min} + A)}{\sin(\frac{1}{2}A)} \qquad \text{............ (16)}$$

Since δm_{min} is a small angle not exceeding 6 degrees and A was of the order of 5 or 7 degrees, then $\sin\frac{1}{2}(\delta m_{min} + A)$ and $\sin(\frac{1}{2}A)$ can be approximated by $\frac{1}{2}(\delta m + A)$ and $\frac{1}{2}A$ radians. Then (16) can be simplified to

$$n = \frac{A + \delta m}{A} \qquad \text{............. (17)}$$

which was the formula used in this experiment.

II.1.2 Materials

The nematic liquid crystals and the binary systems studied in this experiment are listed below.

Pure liquid crystals. (The abbreviated names and catalogue numbers are given in the parentheses.)

p-Azoxyanisole (PAA) was purchased from Aldrich Chemical Co., Inc. (A 9700)

p,p'-di-n-Hexyloxyazoxybenzene (PHAB) was purchased from Frinton Laboratories. (648)
p-(p-Methoxybenzylidene) aminophenyl acetate (MBAPA) was purchased from Frinton Laboratories. (761)

The following liquid crystals were purchased from Eastman Kodak Co.

n-Butyl p-(p-ethoxyphenoxycarbonyl) phenyl carbonate (BEPCPC)(10482)
p-(p-Ethoxyphenylazo) phenyl n-heptanoate (EPP-Hep)(10573)
p-(p-Ethoxyphenylazo) phenyl n-undecylenate (EPPU)(10541)

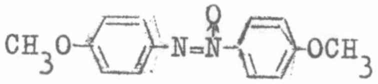
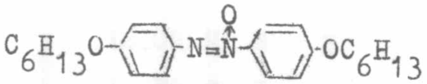
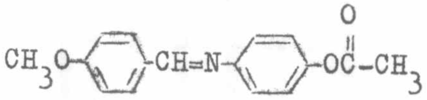
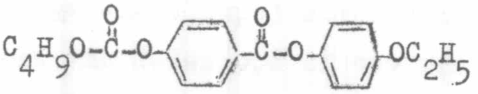
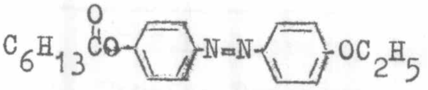
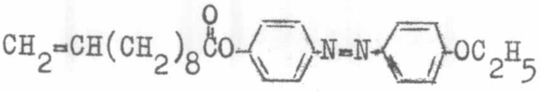
Binary systems of mixed liquid crystals.

(The sources of the following chemicals are the same as those given above.)

1. p-Azoxyanisole (PAA)
   p,p'-di-n-Hexyloxyazoxybenzene (PHAB)
2. p-Azoxyanisole (PAA)
   Butyl p-(p-ethoxyphenoxycarbonyl) phenyl carbonate (BEPCPC)
3. Butyl p-(p-ethoxyphenoxycarbonyl) phenyl carbonate (BEPCPC)
   p-(p-Ethoxyphenylazo) phenyl n-heptanoate (EPP-Hep)
4. p-(p-Ethoxyphenylazo) phenyl n-undecylenate (EPPU)
   p-(p-Methoxybenzylidene) aminophenyl acetate (MBAPA)

The structural formulae of these compounds, their abbreviated names, and their nematic ranges are shown in Table 1.

Table 1 The names, structural formulae, abbreviations, and nematic ranges of six compounds.

Name and Formula	Abbreviation	Nematic Range (°C)
p-Azoxyanisole 	PAA	118.2-134.0
p,p'-di-n-Hexyloxyazoxybenzene 	PHAB	82.0-130.0
p-(p-Methoxybenzylidene) aminophenyl acetate 	MBAPA	83.0-108.9
n-Butyl p-(p-ethoxyphenoxycarbonyl) phenyl carbonate 	BEPCPC	64.5-85.5
p-(p-Ethoxyphenylazo) phenyl n-heptanoate 	EPP-Hep	64.8-116.1
p-(p-Ethoxyphenylazo) phenyl n-undecylenate 	EPPU	65.0-103.2

II.1.3 Preparation of mixtures

Both components of the binary systems of each composition were weighed accurately in a semi-micro test tube. The content was heated to the isotropic phase so that a homogeneous mixture was obtained. Then the liquid was solidified immediately by putting the tube into an ice-water bath. After grinding the solid, the powdered mixture was ready for use.

II.2 Instruments

- REICHERT No. 285167 heating-stage microscope.
- GAERTNER Travelling microscope.
- AO SPENCER SPECTROMETER; American Optical Corporation; Scientific instrument division, Catalog No. 10025.
- Sodium Lamp.

The measurement was carried out by using an arrangement similar to that described in detail by Leelaprute[2]. The heating stage was clamped horizontally between the vertical collimator and the telescope of the spectrometer arranged in the position as shown in Fig. 4

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[2] S.Leelaprute, Refractivity of Nematic Liquid Crystals. M.Sc. Thesis, Department of Chemistry, Mahidol University, Bangkok, Thailand. 1972.

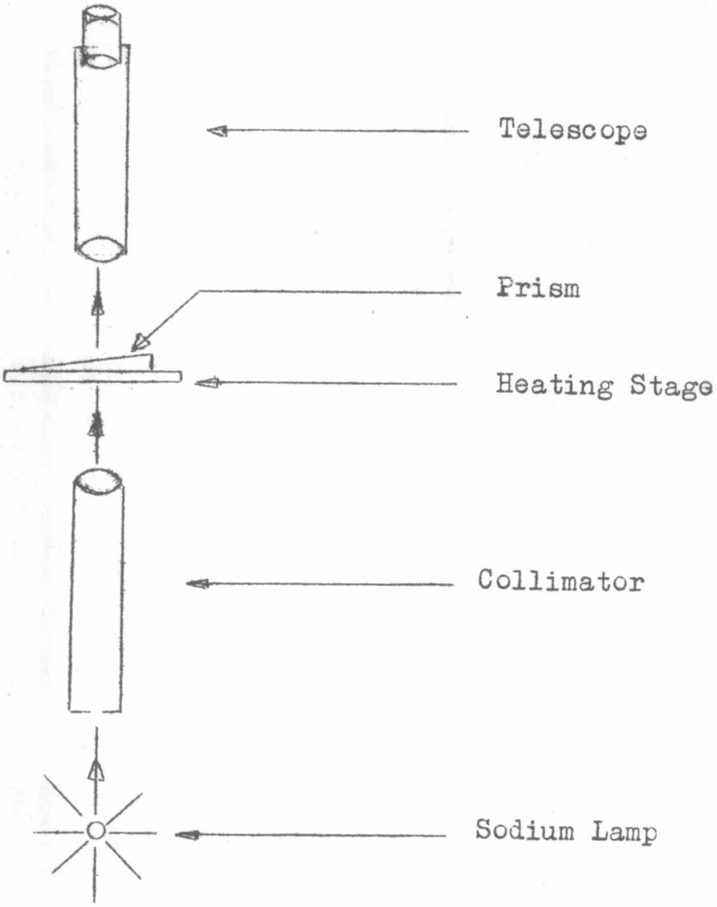

Fig.4 Schematic diagram of apparatus

The small-angle prism formed by two microscope-slide glass plates L_1(2.5x3.0 cm) and L_2(1.5x2.5 cm) is shown in Fig.5. Three cylindrical glass rods a, b, and c were attached by Epoxy Glue to L_1 at positions suitable for making the angle of the prism of the order of 5 degrees. L_2 simply lay on L_1 as indicated in the figure. The small glass rods at a and b were rigidly fixed to the lower glass plate to ensure that the direction of the edge of the prism was parallel to the edge of the glass plate, while the rod at c, the top of which was made hemispherical, determined the value of the angle A of the prism. L_2 had only one point of contact at c. The angle A of the prism was determined by measuring the adjacent and the opposite sides of the angle with a travelling microscope.

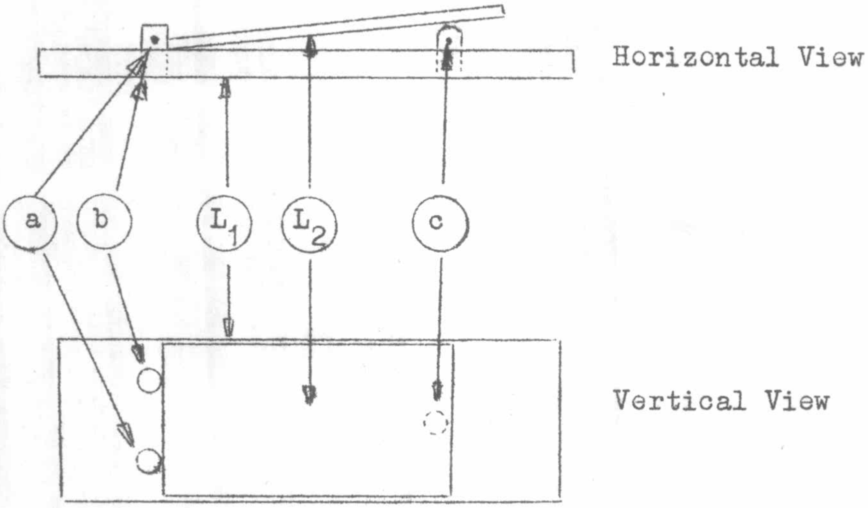

Fig.5 Schematic diagram of horizontal and vertical projections of the prism.

The prism was placed on an electric heating stage which had a small hole in it through which the light could be passed, the whole being mounted on the steel ring as illustrated in Fig.6. The steel ring which was attached to a steel rod was mounted at the center of a large pulley. The string was wound on the large pulley to a small pulley, a controlled rotation of which would make the heating stage and the prism rotate uniformly in any desired direction.

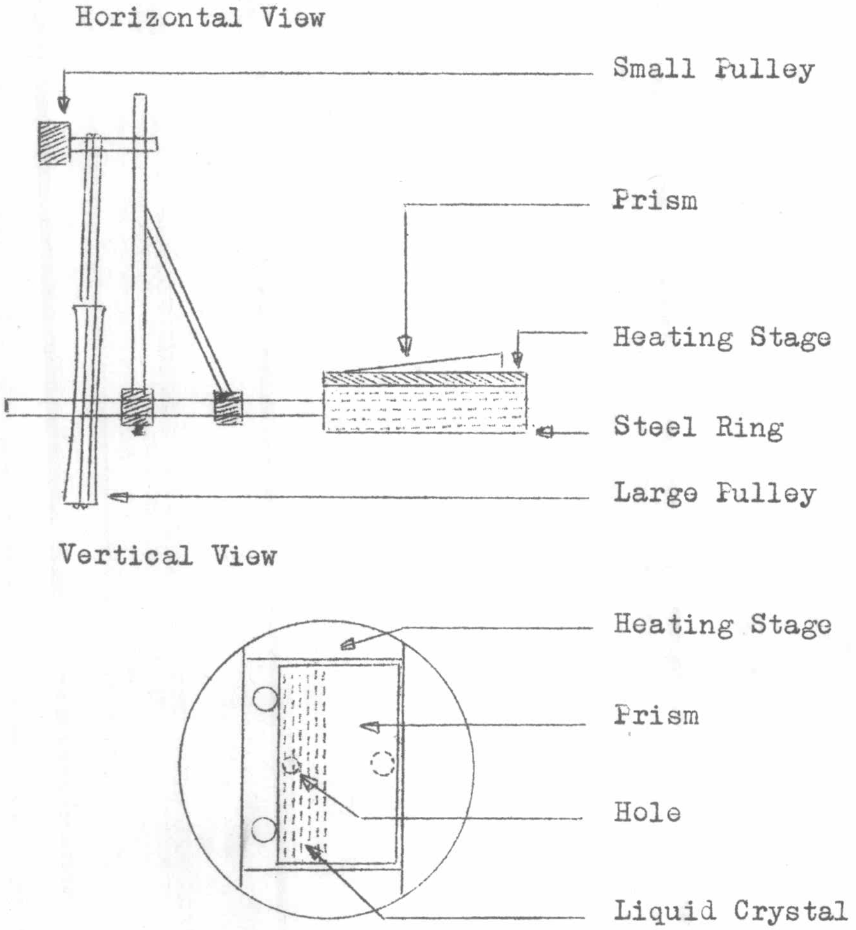

Fig.6 Schematic diagram of horizontal and vertical projections of liquid crystal prism mounted on rotating instrument.

II.3 Observation of Birefringence

The glass plates used for making the prism were cleaned with acetone and a liquid crystal was placed in the manner already described. It is known that the refractive index in the unoriented turbid medium cannot be measured. However, the prism of a nematic liquid crystal thus constructed, with molecules in the carefully oriented state, is optically clear enough to allow measurement to be made of the two principal indices of refraction. The oriented uniaxial state could conveniently be obtained as a consequence of the action of the walls of the glass plates, the internal faces of which had previously been rubbed parallel to the edge of the prism. Under this action the molecules of the nematic liquid crystal became oriented in a direction parallel to the refracting edge **A.** This liquid crystal prism was essentially equivalent to a prism cut from a positive uniaxial crystal, with its edge parallel to the optic axis. The temperature of the liquid crystal sample was read directly from the thermometer attached to the heating stage. However, it was not the actual temperature and had to be corrected, as the sample was not in a closed oven. It was found that the directly observed temperatures were about 2 degrees higher than the actual values that have been reported in this work. The two spectral lines caused by the birefringence were observed separately, and the angles of minimum deviation (δm) of the ordinary ray and extraordinary ray were measured at various temperatures.

II.4 Results

The accuracy of the index of refraction measurements for the nematic liquid crystals and their mixtures is to within ±0.002. The refractive index of the ordinary ray (with electric vector normal to the optic axis), the index of the extraordinary ray (with electric vector parallel to the optic axis), and the average index are designated by n_o, n_e and $\bar{n}$, respectively; n_i indicates the refractive index of the isotropic liquid. The refractive indices n_o, n_e, n_i and $\bar{n}$ at various temperatures of the six nematic compounds and the four binary systems of mixed liquid crystals are shown in Tables 2, 3, 4 and 5.

The relationships between the ordinary refractive index (n_o), the extraordinary refractive index (n_e) and the relative temperature ($t_f - t$) of the four binary systems are shown in Figs. 7,8,9,10,11, 12,13 and 14. The contours of the extraordinary refractive indices in the temperature-composition plane of these four binary systems are demonstrated in Figs. 15,16,17 and 18. The phase boundaries of the nematic regions in the temperature-composition planes are based on the experimental results of Pdungsap[3] and Buanam-om[4]. Figs. 19,20,21 and 22 show the perspective plots of the refractive indices n_e, n_o, n_i of the binary systems in the temperature-composition planes. The temperature dependence of the refractive indices n_e, n_o, n_i and $\bar{n}$ of six compounds and their mixtures are illustrated in Figs. 23, 24, 25, 26, 27, 28 and 29. The double refraction of the four binary systems are shown in Figs. 30,31,32, and 33. Plots of $\ln\left[(\bar{n}^2-1)/(\bar{n}^2+2)\right]$ versus temperature are given in Figs. 34,35,36 and 37.

II.5 Limits of Inaccuracies

Impurities of the substances would cause appreciable errors, so all the substances used were recrystallized several times. The substances were weighed on an analytical balance which could be read to within ± 0.0001 gm. One trouble that arose in weighing was that the sensitivity and accuracy of the balance were not constant throughout the whole scale.

The thermometer attached to the heating stage could be read accurately to within 1 degree interval. The temperature readings were approximately two degrees higher than the actual values, and all the temperatures reported in this work have already been corrected.

The value of the angle A of the liquid crystal prism was obtained by measuring the adjacent and the opposite sides of the

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[3] L.Pdungsap, Phase Equilibria of Mixed Liquid Crystals, M.Sc. Thesis, Department of Chemistry, Mahidol University, Bangkok, Thailand, 1972

[4] C.Buanam-om, Thermal Properties and Phase Behaviors of Liquid Crystals, M.Sc. Thesis, Department of Chemistry, Mahidol University, Bangkok, Thailand, 1973

prism with the aid of a travelling microscope, which could be read to within the limit of error of ± 5μm. However, L_1 and L_2 were not fixed and could be moved relative to each other. It was difficult to obtain a constant prism angle; so the results of the measurement at each side of the prism were averaged. Also, in the experiments, when the sample was placed between L_1 and L_2, it lifted L_1 slightly relative to L_2. The amount of this lifting could vary from sample to sample, and the accuracy of the prism angle used for each system is accordingly affected.

The minimum deviation angle was measured with the aid of the spectrometer, which could be read to within a limit of error of ± 0.5 minute of arc. The backlash in the telescope movement could also have caused some slight error in the measurement. So, measurements of the extraordinary and isotropic spectral lines were first measured; then the sample was cooled down to the solid phase and on re-heating the ordinary spectral line was measured. By using this technique of measurement, the minimum deviation angles for the nematic compounds and their mixtures are probably in error of only up to a few minutes of arc.

Table 2. The refractive indices of the mixtures of PAA and PHAB

Typical $A = 6^{\circ}\ 4.0'$

τ = mole fraction of PAA in the mixture

(a) Pure PHAB, $t_f = 130.0^{\circ}C$

Temperature ($^{\circ}C$)	n_o	n_e	n_i	$\bar{n}$
86	1.472	1.623		1.523
91		1.618		1.522
98	1.475	1.615		1.523
103		1.609		1.520
107	1.478	1.601		1.519
112		1.590		1.515
116	1.480	1.585		1.515
120		1.579		1.513
124	1.483	1.574		1.513
128		1.568		1.511
132			1.511	
138			1.508	
145			1.505	

(b) $\tau = 0.10$, $t_f = 127.0^{\circ}C$

Temperature ($^{\circ}C$)	n_o	n_e	n_i	$\bar{n}$
81	1.489	1.642		1.541
85		1.640		1.540
90	1.491	1.631		1.538
93		1.626		1.537
98	1.494	1.620		1.536
103		1.612		1.534
107	1.497	1.601		1.532
112		1.593		1.529
115	1.502	1.587		1.530
117		1.582		1.529
120	1.506	1.576		1.529
125		1.565		1.525
127			1.527	
135			1.524	
145			1.521	

(c) τ = 0.20 , t_f = 125.5 °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
80	1.491	1.651		1.545
85		1.645		1.544
88	1.494	1.642		1.544
91		1.637		1.543
96	1.497	1.634		1.544
100		1.629		1.542
105	1.500	1.623		1.542
110		1.615		1.539
115	1.502	1.604		1.536
120		1.596		1.533
124	1.506	1.587		1.533
127			1.532	
135			1.530	
145			1.527	

(d) τ = 0.30 , t_f = 125.0 °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
86	1.497	1.678		1.555
90		1.673		1.553
95	1.500	1.662		1.555
100		1.653		1.552
105	1.502	1.645		1.551
110		1.640		1.549
115	1.506	1.634		1.549
120	1.508	1.629		1.549
124	1.511	1.620		1.547
127			1.546	
132			1.543	
140			1.541	

(e) $\alpha = 0.40$, $t_f = 126$ °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
90	1.500	1.692		1.566
95		1.689		1.565
100	1.502	1.686		1.565
105		1.678		1.562
110	1.508	1.670		1.563
115		1.662		1.560
120	1.511	1.656		1.560
125	1.513	1.648		1.559
127			1.560	
140			1.557	
148			1.554	

(f) $\alpha = 0.50$, $t_f = 124$ °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
97	1.511	1.714		1.581
100		1.708		1.579
105	1.513	1.700		1.577
110		1.692		1.574
115	1.519	1.684		1.575
120		1.675		1.572
125			1.577	
130			1.568	
138			1.565	

(g) $\tau = 0.60$, $t_f = 122.5$ °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
104	1.521	1.728		1.592
106		1.719		1.589
108		1.717		1.588
112	1.524	1.708		1.587
115		1.700		1.584
118		1.686		1.579
120	1.530	1.681		1.581
124			1.579	
130			1.574	
135			1.571	

(h) $\tau = 0.70$, $t_f = 123$ °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
108	1.530	1.741		1.603
110		1.730		1.599
115	1.535	1.725		1.600
117		1.719		1.598
120	1.541	1.711		1.599
122		1.706		1.597
125			1.596	
131			1.593	
140			1.590	

(i) $\tau = 0.80$, $t_f = 126$ °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
112	1.543	1.771		1.622
114		1.766		1.620
118	1.546	1.761		1.620
120		1.752		1.617
124	1.549	1.747		1.615
125	1.549	1.739		1.614
127			1.612	
135			1.609	
140			1.604	

(j) $\alpha = 0.90$, $t_f = 128$ °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
117	1.650	1.788		1.639
120		1.782		1.637
122	1.563	1.774		1.636
124		1.766		1.633
126	1.565	1.758		1.631
129			1.629	
134			1.626	
140			1.620	

(k) Pure PAA, $t_f = 134$ °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
119	1.563	1.846		1.662
121		1.837		1.659
123	1.565	1.829		1.657
127	1.565	1.821		1.654
129	1.568	1.810		1.652
132		1.802		1.649
133	1.571	1.799		1.650
136			1.645	
140			1.640	
147			1.637	

Table 3. The refractive indices of the mixtures of PAA and BEPCPC

Typical A = $6^\circ\ 29.5'$

τ = mole fraction of PAA in the mixture

(a) Pure BEPCPC, $t_f = 85.5^\circ C$

Temperature ($^\circ$C)	n_o	n_e	n_i	$\bar{n}$
65	1.544	1.706		1.599
68		1.703		1.598
72		1.698		1.596
75		1.688		1.593
78	1.546	1.682		1.592
80		1.677		1.590
83		1.670		1.588
85	1.549	1.664		1.588
87			1.585	
94			1.582	
100			1.580	

(b) $\tau = 0.10$, $t_f = 87^\circ C$

Temperature ($^\circ$C)	n_o	n_e	n_i	$\bar{n}$
65	1.544	1.711		1.601
68		1.708		1.600
70		1.706		1.599
73		1.703		1.598
75		1.698		1.596
78	1.546	1.693		1.596
80		1.688		1.594
83		1.682		1.592
85		1.675		1.589
88	1.549	1.667		1.589
89			1.587	
95			1.585	
102			1.582	

(c) $\tau = 0.15$, $t_f = 87.5$ °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
65	1.544	1.716		1.603
68		1.713		1.602
70		1.711		1.601
73	1.544	1.708		1.600
75		1.706		1.599
78	1.546	1.700		1.598
80		1.695		1.597
83		1.690		1.595
85	1.549	1.682		1.594
88			1.590	
100			1.587	
107			1.582	

(d) $\tau = 0.20$, $t_f = 89.5$ °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
62	1.544	1.721		1.604
65		1.718		1.603
68		1.716		1.603
72	1.546	1.711		1.602
75		1.706		1.600
78		1.700		1.598
80	1.549	1.695		1.599
83		1.690		1.597
85		1.685		1.595
87	1.551	1.680		1.594
91			1.593	
98			1.590	
103			1.587	
115			1.582	

(e) $\tau = 0.25$, $t_f = 89.5\ ^{o}C$

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
65	1.546	1.724		1.607
68		1.721		1.606
72		1.718		1.605
75	1.549	1.713		1.605
78		1.708		1.603
80		1.703		1.601
83	1.551	1.698		1.601
85		1.693		1.599
87		1.688		1.597
89	1.554	1.682		1.597
91			1.595	
99			1.593	
105			1.590	

(f) $\tau = 0.30$, $t_f = 91.5\ ^{o}C$

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
76	1.546	1.716		1.604
78		1.713		1.603
80		1.708		1.601
82	1.549	1.700		1.600
85		1.695		1.599
88		1.685		1.595
90	1.551	1.675		1.593
94			1.590	
100			1.585	
105			1.582	

(g) $\tau = 0.35$, $t_f = 92.6\ ^{o}C$

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
80	1.546	1.718		1.605
84		1.716		1.604
88		1.708		1.601
90	1.549	1.700		1.600
92		1.695		1.599
93	1.551	1.688		1.597
96			1.595	
102			1.590	
108			1.587	

(h) τ = 0.40 , t_f = 95 °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
84	1.549	1.721		1.608
87		1.716		1.606
90	1.551	1.711		1.606
92		1.706		1.604
94	1.554	1.698		1.603
100			1.600	
105			1.598	
113			1.595	

(i) τ = 0.45 , t_f = 95.5 °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
87	1.549	1.726		1.609
88		1.724		1.609
89		1.721		1.608
90	1.551	1.718		1.608
91		1.716		1.607
92		1.713		1.606
93		1.708		1.604
94	1.554	1.703		1.604
95		1.693		1.602
96		1.688		1.599
99			1.598	
104			1.593	
110			1.587	

(j) τ = 0.50 , t_f = 99 °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
95	1.551	1.711		1.606
96		1.708		1.604
97		1.706		1.604
98		1.698		1.601
99	1.554	1.693		1.601
100		1.688		1.599
103			1.595	
109			1.587	
113			1.582	

(k) τ = 0.55 , t_f = 102 °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
100	1.554	1.737		1.614
101		1.726		1.613
102	1.557	1.718		1.612
103			1.611	
108			1.605	
114			1.598	

(l) τ = 0.60 , t_f = 105 °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
103	1.557	1.744		1.621
104		1.739		1.619
105	1.559	1.734		1.619
106			1.618	
111			1.613	
116			1.608	
120			1.605	

(m) τ = 0.65 , t_f = 106 °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
102	1.557	1.749		1.623
103		1.744		1.621
104	1.559	1.739		1.621
105		1.731		1.618
107			1.616	
111			1.608	
116			1.606	

(n) τ = 0.70 , t_f = 109.5 °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
105	1.557	1.767		1.629
106		1.757		1.626
107		1.749		1.623
108	1.559	1.739		1.621
110			1.616	
113			1.608	
116			1.600	

(o) $\tau = 0.75$, $t_f = 114$ °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
105	1.557	1.782		1.635
108	1.559	1.774		1.633
110		1.767		1.630
114	1.562	1.757		1.629
115			1.629	
120			1.623	
128			1.618	

(p) $\tau = 0.80$, $t_f = 117$ °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
110	1.559	1.790		1.639
112		1.782		1.636
114		1.777		1.634
115	1.562	1.767		1.633
120			1.626	
125			1.618	
130			1.613	

(q) $\tau = 0.85$, $t_f = 117.9$ °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
112	1.562	1.818		1.651
114	1.564	1.810		1.649
115		1.800		1.646
118	1.567	1.790		1.644
120			1.641	
125			1.636	
130			1.631	

(r) $\tau = 0.90$, $t_f = 127$ °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
115	1.562	1.820		1.652
118		1.810		1.648
120	1.564	1.797		1.645
123	1.567	1.782		1.641
125	1.569	1.777		1.641
129			1.636	
135			1.629	
140			1.621	

(s) Pure PAA , $t_f = 135.5$ °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
120	1.562	1.838		1.658
123		1.831		1.656
125	1.564	1.820		1.653
128		1.810		1.649
130	1.567	1.800		1.648
133		1.790		1.644
134	1.569	1.779		1.641
137			1.639	
140			1.636	
144			1.631	

Table 4. The refractive indices of the mixtures of BEPCPC and EPP-Hep

Typical $A = 5^\circ\ 54.0'$

τ = mole fraction of BEPCPC in the mixture

(a) Pure EPP-Hep, $t_f = 116.1^\circ C$

Temperature ($^\circ$C)	n_o	n_e	n_i	$\bar{n}$
65	1.440	1.729		1.540
70		1.720		1.538
75	1.443	1.714		1.538
80		1.706		1.535
85		1.700		1.533
90	1.446	1.692		1.532
95		1.686		1.529
100	1.449	1.677		1.528
105	1.451	1.663		1.528
110		1.646		1.526
113	1.454	1.635		1.526
115	1.460	1.621		1.524
118			1.524	
125			1.522	
133			1.520	

(b) $\tau = 0.10$, $t_f = 112.2^\circ C$

Temperature ($^\circ$C)	n_o	n_e	n_i	$\bar{n}$
64	1.451	1.731		1.549
70		1.728		1.548
75		1.723		1.546
80	1.454	1.711		1.544
85		1.706		1.542
90		1.697		1.539
95		1.692		1.537
100	1.457	1.680		1.534
105		1.672		1.531
110		1.658		1.526
112	1.460	1.649		1.525
116			1.523	
123			1.522	
131			1.520	

(c) $\tau = 0.20$; $t_f = 108.4\ ^{\circ}\mathrm{C}$

Temperature ($^{\circ}$C)	n_o	n_e	n_i	$\bar{n}$
60	1.443	1.709		1.536
65		1.703		1.534
70		1.700		1.533
75	1.446	1.697		1.534
80		1.689		1.531
85	1.449	1.683		1.531
90		1.675		1.528
95	1.451	1.663		1.524
100		1.655		1.521
103	1.454	1.646		1.520
105		1.638		1.517
110			1.514	
119			1.511	
127			1.509	

(d) $\tau = 0.30$; $t_f = 105.9\ ^{\circ}\mathrm{C}$

Temperature ($^{\circ}$C)	n_o	n_e	n_i	$\bar{n}$
60	1.446	1.703		1.536
65		1.700		1.535
70	1.449	1.692		1.534
75		1.686		1.531
80		1.675		1.528
85	1.451	1.666		1.525
90		1.658		1.522
95		1.649		1.519
100	1.454	1.641		1.518
104		1.624		1.512
105		1.621		1.511
106	1.457	1.615		1.511
109			1.511	
117			1.509	
125			1.507	

(e) $\tau = 0.40$; $t_f = 101.7\ ^{o}C$

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
55	1.454	1.700		1.540
60		1.694		1.538
65		1.686		1.535
70	1.457	1.677		1.533
75		1.675		1.532
80		1.666		1.529
85		1.661		1.528
90	1.460	1.646		1.524
95		1.635		1.520
100		1.627		1.517
102		1.621		1.515
104	1.468	1.610		1.516
105			1.516	
113			1.514	
125			1.511	

(f) $\tau = 0.50$; $t_f = 99.2\ ^{o}C$

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
55	1.460	1.669		1.532
60		1.663		1.530
63		1.661		1.530
65		1.655		1.527
70		1.646		1.524
75	1.463	1.641		1.524
80		1.635		1.522
83		1.629		1.520
85		1.627		1.519
88		1.624		1.518
90	1.466	1.618		1.518
93		1.615		1.518
95		1.612		1.516
96		1.610		1.515
97		1.604		1.513
100	1.468	1.596		1.511
101			1.509	
110			1.507	
120			1.505	

(g) $\alpha = 0.60$; $t_f = 94.0$ °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
60	1.514	1.720		1.585
65		1.717		1.584
70		1.706		1.580
75		1.697		1.577
80	1.516	1.692		1.576
85		1.689		1.575
90		1.677		1.571
93		1.666		1.567
95	1.522	1.661		1.569
97			1.564	
104			1.562	
115			1.560	

(h) $\alpha = 0.70$; $t_f = 93.4$ °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
60	1.539	1.765		1.617
65		1.759		1.615
70	1.542	1.754		1.615
75		1.745		1.612
80		1.740		1.610
85	1.545	1.731		1.609
90		1.717		1.604
93		1.714		1.603
94	1.546	1.706		1.600
98			1.601	
106			1.598	
114			1.597	

(i) $\tau = 0.80$; $t_f = 91.1\ ^{o}C$

Temperature (^{o}C)	n_o	n_e	n_i	$\bar{n}$
60	1.564	1.779		1.638
65		1.771		1.635
70		1.762		1.632
75	1.567	1.751		1.630
80		1.740		1.626
85		1.731		1.623
90	1.570	1.714		1.619
92			1.615	
100			1.612	
110			1.610	

(j) $\tau = 0.90$; $t_f = 87.1\ ^{o}C$

Temperature (^{o}C)	n_o	n_e	n_i	$\bar{n}$
65	1.528	1.706		1.589
70		1.697		1.586
75	1.531	1.692		1.586
80		1.683		1.583
85	1.533	1.675		1.581
87		1.663		1.577
89			1.567	
100			1.564	
109			1.562	

(k) Pure BEPCPC ; $t_f = 85.5\ ^{o}C$

Temperature (^{o}C)	n_o	n_e	n_i	$\bar{n}$
65	1.545	1.700		1.598
70		1.694		1.596
75		1.686		1.593
80		1.677		1.589
85	1.550	1.666		1.589
87			1.590	
94			1.587	
99			1.583	

Table 5. The refractive indices of the mixtures of EPPU and MBAPA

Typical $A = 5^\circ\ 24.5'$

τ = mole fraction of EPPU in the mixture

(a) Pure MBAPA, $t_f = 103.2^\circ C$

Temperature ($^\circ C$)	n_o	n_e	n_i	$\bar{n}$
85	1.511	1.838		1.627
88		1.832		1.624
90	1.514	1.825		1.624
93		1.816		1.620
95	1.517	1.810		1.620
98		1.801		1.617
100	1.520	1.788		1.614
105			1.610	
113			1.603	
120			1.597	
127			1.591	

(b) $\tau = 0.10$, $t_f = 104.6^\circ C$

Temperature ($^\circ C$)	n_o	n_e	n_i	$\bar{n}$
80	1.511	1.832		1.624
85		1.825		1.622
90		1.813		1.617
95	1.514	1.801		1.615
100		1.779		1.607
105	1.517	1.761		1.602
108			1.607	
118			1.603	
128			1.600	

(c) τ = 0.15 ; t_f = 104.0 °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
75	1.508	1.838		1.625
80		1.825		1.620
85	1.511	1.810		1.616
90		1.798		1.612
95	1.514	1.782		1.608
100	1.520	1.751		1.600
105			1.597	
110			1.594	
115			1.591	
120			1.588	

(d) τ = 0.20 ; t_f = 103.6 °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
75	1.499	1.825		1.614
80		1.816		1.611
85	1.502	1.810		1.611
90		1.788		1.602
95	1.505	1.779		1.601
100		1.764		1.595
104			1.591	
108			1.588	
113			1.585	
118			1.582	

(e) τ = 0.25 ; t_f = 103.5 °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
70	1.496	1.832		1.615
75		1.819		1.610
80	1.499	1.810		1.609
85		1.801		1.605
90	1.502	1.779		1.599
95		1.758		1.591
100	1.505	1.736		1.585
104			1.582	
108			1.579	
111			1.576	
125			1.573	

(f) τ = 0.30 ; t_f = 103.7 °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
70	1.493	1.825		1.611
75		1.816		1.607
80	1.496	1.807		1.606
85		1.798		1.602
90		1.776		1.594
95	1.499	1.764		1.592
100		1.758		1.589
105	1.502	1.745		1.587
108			1.582	
112			1.579	
116			1.576	
120			1.573	

(g) τ = 0.35 ; t_f = 102.5 °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
70	1.489	1.801		1.599
75		1.798		1.598
80		1.791		1.595
85	1.493	1.782		1.594
90		1.770		1.590
95		1.758		1.586
100	1.496	1.742		1.582
106			1.582	
110			1.579	
114			1.576	
119			1.573	

(h) τ = 0.40 ; t_f = 102.4 °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
65	1.483	1.801		1.595
70		1.798		1.594
75		1.791		1.592
80		1.785		1.589
85	1.486	1.776		1.588
90		1.764		1.583
95	1.489	1.751		1.581
100		1.742		1.577
102	1.493	1.733		1.577
105			1.576	
110			1.573	
115			1.570	
121			1.567	

(i) τ = 0.45 ; t_f = 103.0 °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
65	1.483	1.798		1.594
70		1.791		1.592
75		1.779		1.587
80		1.770		1.584
85		1.761		1.580
90	1.486	1.758		1.581
95		1.745		1.577
100		1.724		1.569
102	1.489	1.711		1.566
106			1.563	
110			1.560	
118			1.557	
122			1.554	

(j) $\tau = 0.50$; $t_f = 104.3\ ^{o}C$

Temperature (^{o}C)	n_o	n_e	n_i	$\bar{n}$
65	1.486	1.804		1.598
70		1.798		1.596
75		1.782		1.590
80		1.773		1.587
85	1.489	1.758		1.583
90		1.755		1.582
95		1.739		1.576
100	1.493	1.724		1.573
105			1.570	
109			1.567	
115			1.563	
120			1.560	

(k) $\tau = 0.55$; $t_f = 105.0\ ^{o}C$

Temperature (^{o}C)	n_o	n_e	n_i	$\bar{n}$
65	1.489	1.807		1.601
70		1.798		1.598
75		1.779		1.591
80		1.770		1.588
85	1.493	1.761		1.587
90		1.751		1.583
95		1.736		1.577
100	1.496	1.711		1.570
106			1.567	
110			1.563	
115			1.560	
122			1.557	

(l) $\tau = 0.60$; $t_f = 105.4$ °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
65	1.493	1.810		1.605
70		1.798		1.600
75	1.496	1.782		1.596
80		1.776		1.594
85		1.764		1.590
90	1.499	1.758		1.589
95		1.742		1.583
100	1.502	1.724		1.579
105	1.508	1.711		1.578
107			1.576	
112			1.573	
117			1.570	
120			1.567	

(m) $\tau = 0.65$; $t_f = 105.5$ °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
65	1.489	1.804		1.600
70		1.795		1.597
75		1.785		1.593
80		1.779		1.591
85	1.493	1.773		1.591
90		1.761		1.587
95	1.496	1.755		1.586
100		1.714		1.571
105	1.499	1.684		1.563
108			1.557	
115			1.554	
121			1.551	
125			1.548	

(a) $\tau = 0.70$; $t_f = 105.6$ °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
65	1.486	1.816		1.603
70		1.801		1.597
75	1.489	1.791		1.595
80		1.782		1.592
85		1.773		1.589
90	1.493	1.761		1.587
95		1.746		1.581
100	1.496	1.736		1.579
105	1.502	1.708		1.573
110			1.570	
115			1.567	
120			1.563	
125			1.560	

(b) $\tau = 0.75$; $t_f = 106.0$ °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
65	1.480	1.828		1.604
70		1.819		1.600
75		1.807		1.596
80		1.801		1.594
85	1.483	1.788		1.590
90		1.776		1.586
95	1.486	1.761		1.582
100		1.745		1.577
105	1.493	1.724		1.573
109			1.567	
115			1.563	
120			1.557	
127			1.554	
133			1.551	

(p) $\tau = 0.80$; $t_f = 106.5$ °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
65	1.477	1.816		1.598
70		1.807		1.594
75		1.798		1.591
80	1.480	1.795		1.591
85		1.779		1.585
90		1.767		1.581
95	1.483	1.758		1.579
100		1.742		1.573
105	1.493	1.727		1.574
110			1.573	
115			1.570	
120			1.567	
126			1.563	

(q) $\tau = 0.85$; $t_f = 107.0$ °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
65	1.473	1.810		1.593
70		1.807		1.592
75	1.477	1.798		1.591
80		1.788		1.587
85		1.779		1.583
90		1.764		1.578
95	1.480	1.758		1.577
100		1.742		1.571
105	1.489	1.733		1.574
110			1.570	
115			1.567	
120			1.563	
124			1.560	

(r) τ = 0.90 ; t_f = 107.6 °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
65	1.467	1.807		1.588
70		1.801		1.586
75		1.798		1.584
80		1.791		1.582
85	1.473	1.782		1.582
90		1.776		1.580
95		1.761		1.574
100	1.477	1.745		1.571
105	1.483	1.736		1.571
109			1.567	
115			1.563	
120			1.560	
125			1.557	

(s) Pure EPPU ; t_f = 108.9 °C

Temperature (°C)	n_o	n_e	n_i	$\bar{n}$
65	1.483	1.810		1.599
70		1.803		1.596
75		1.799		1.594
80		1.795		1.593
85	1.486	1.788		1.592
90		1.779		1.589
95		1.764		1.583
100	1.489	1.751		1.581
105	1.493	1.742		1.580
110			1.579	
115			1.576	
122			1.573	
127			1.570	

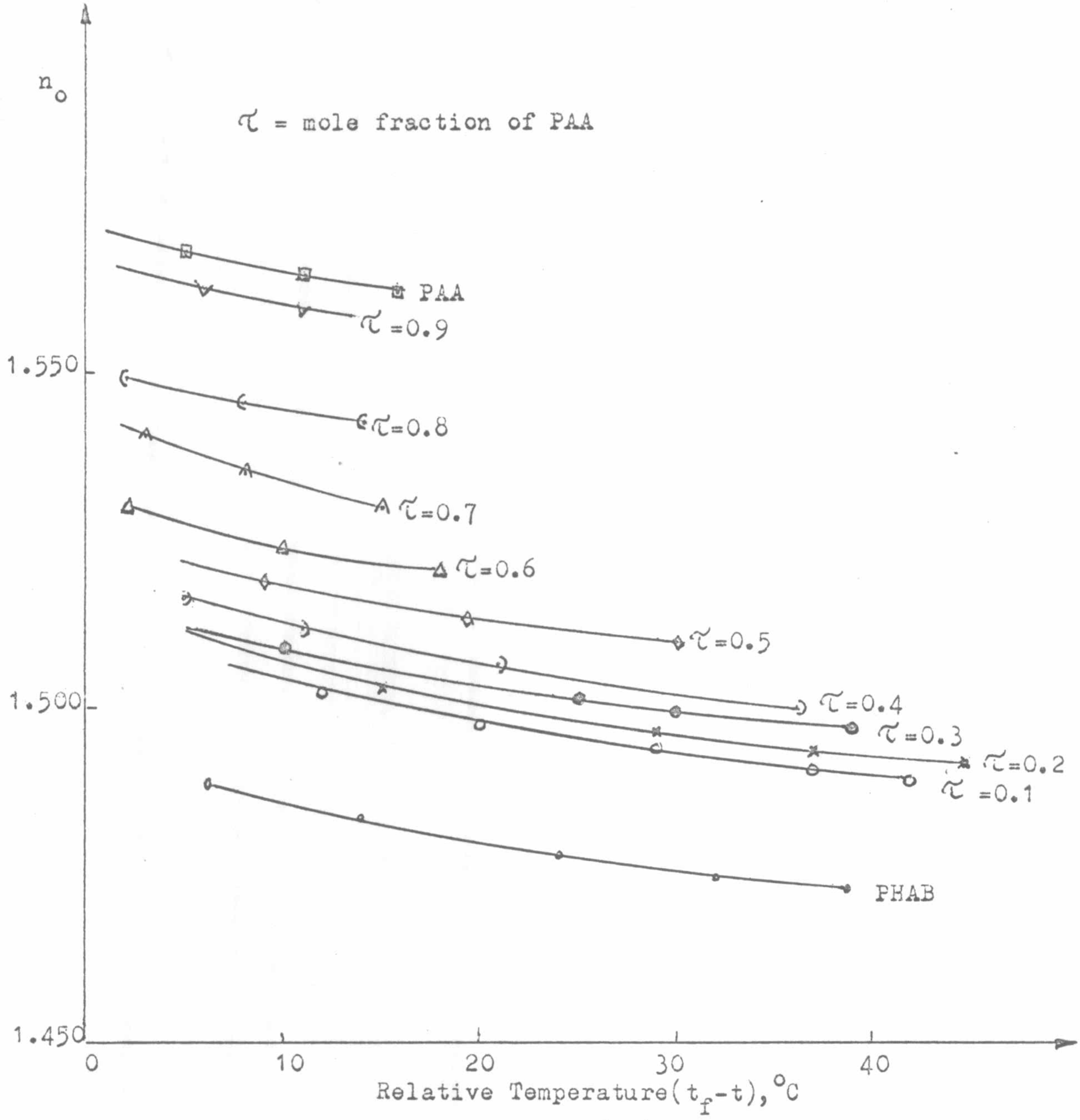

Fig.7 The ordinary refractive index(n_o) of PAA,PHAB and their mixtures plotted against the relative temperature.

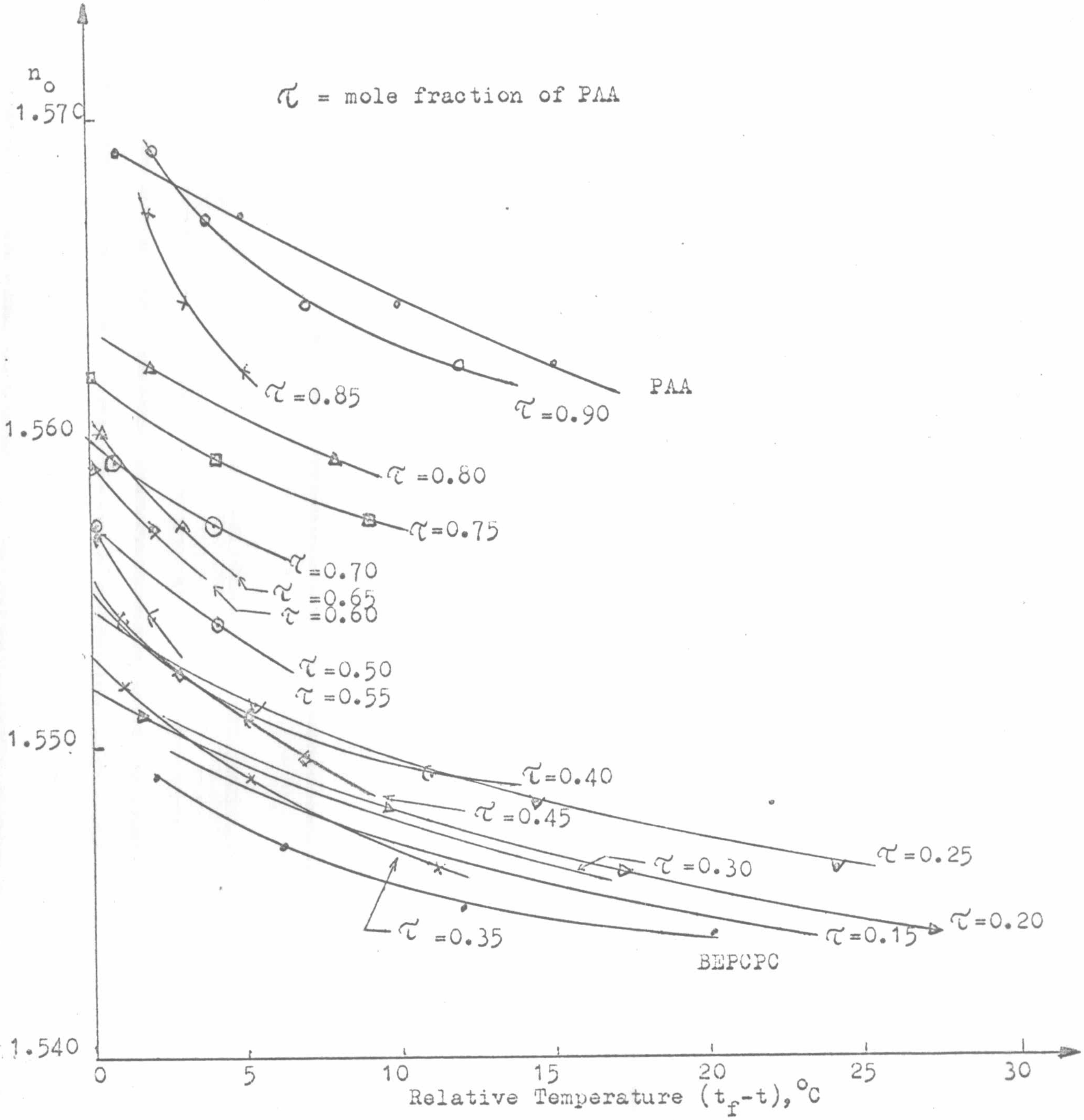

Fig.8 The ordinary refractive index(n_o) of PAA, BEPCPC and their mixtures plotted against the relative temperature.

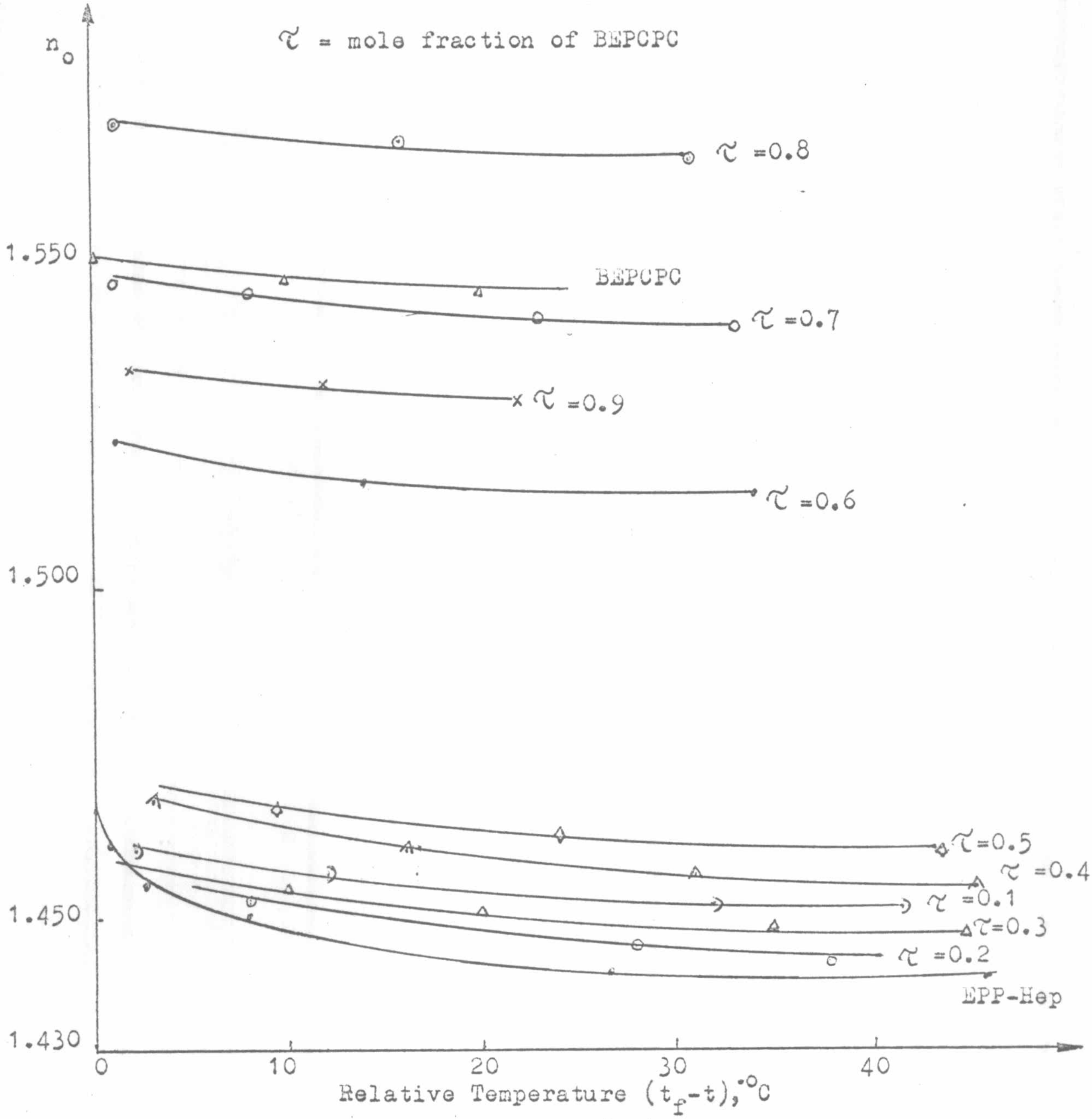

Fig.9 The ordinary refractive index(n_o) of EPP-Hep, BEPCPC and their mixtures plotted against the relative temperature.

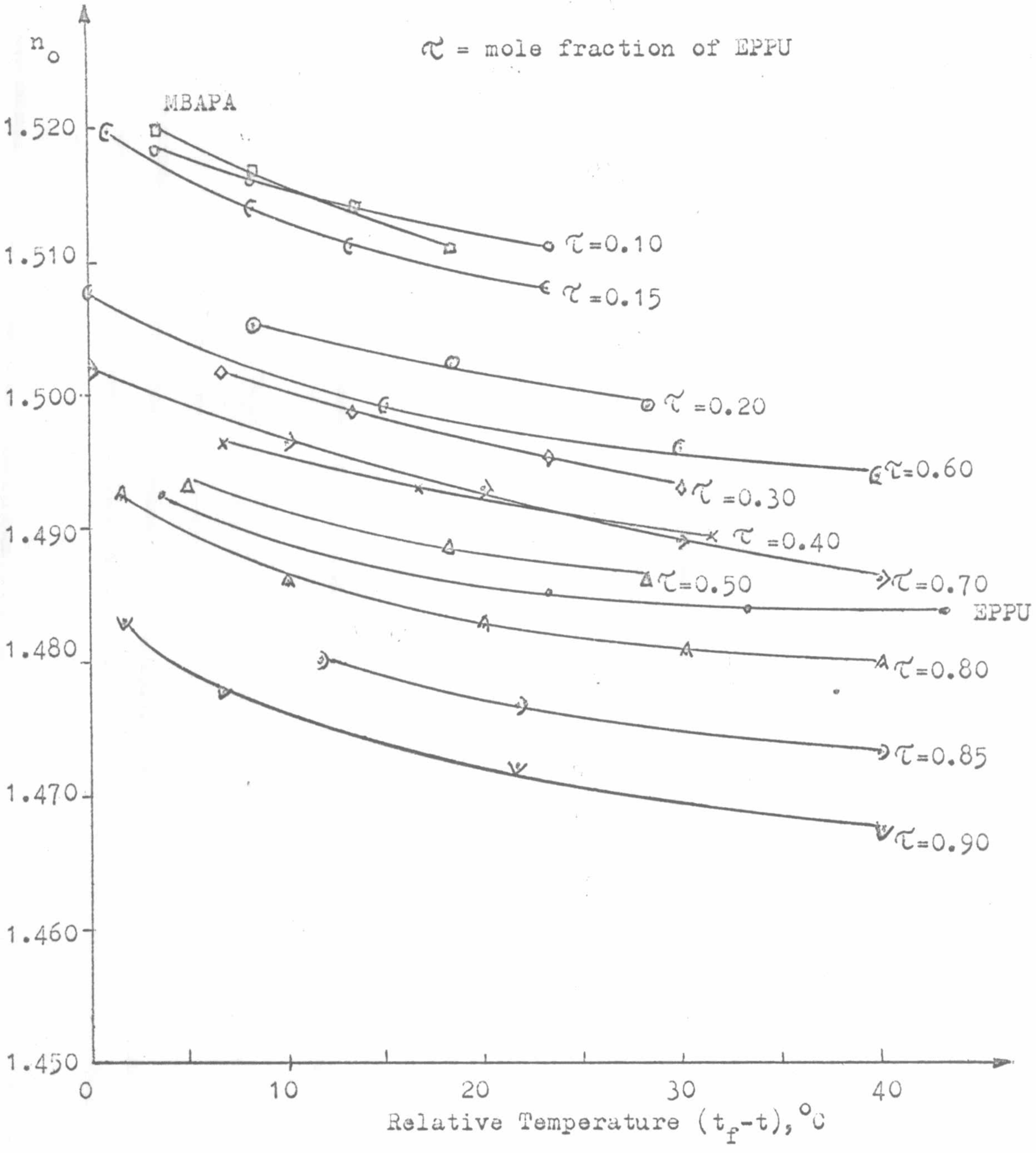

Fig. 10 The ordinary refractive index (n_o) of EPPU, MBAPA and their mixtures plotted against the relative temperature.

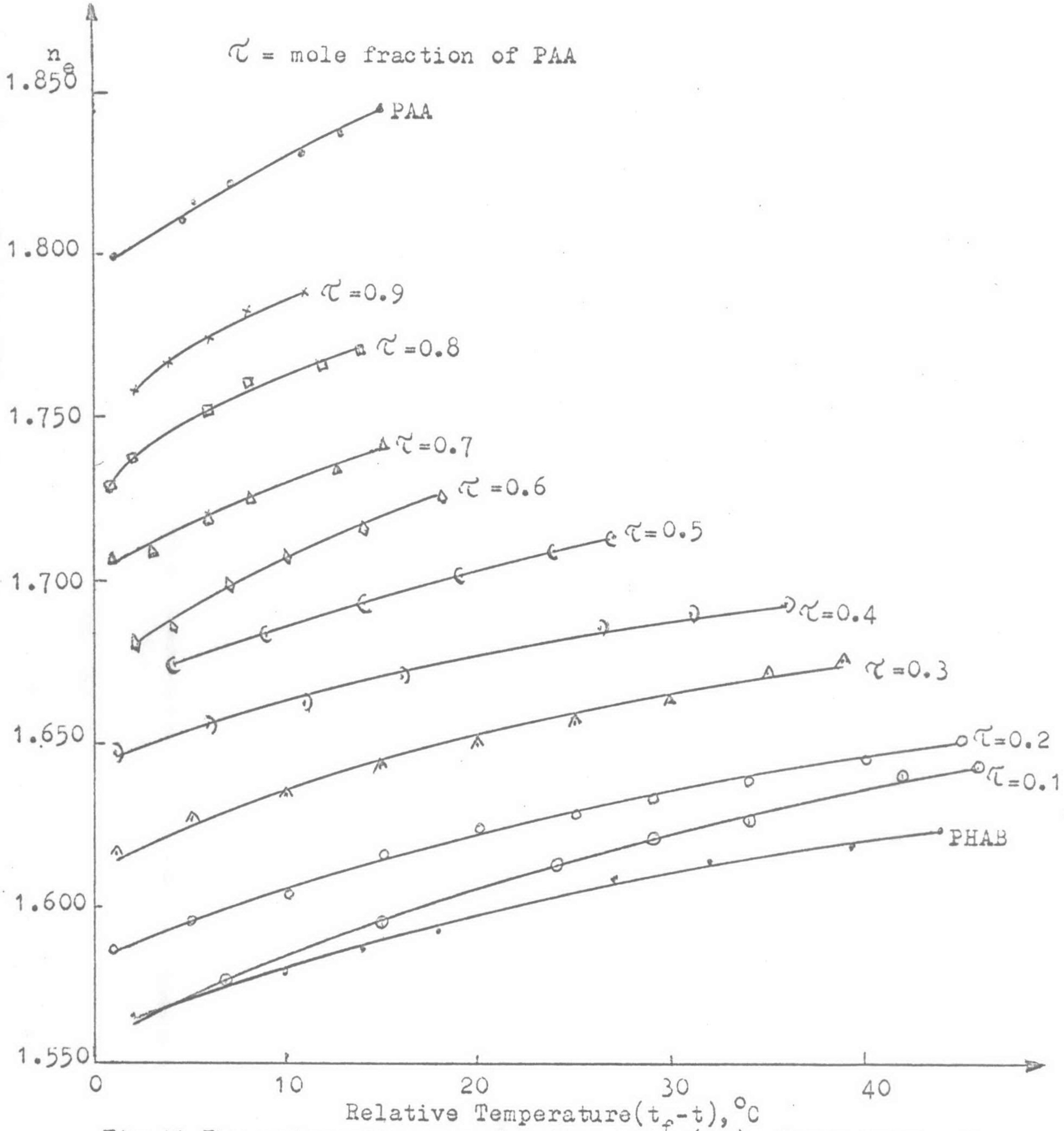

Fig.11 The extraordinary refractive index(n_e) of PAA,PHAB and their mixtures plotted against the relative temperature.

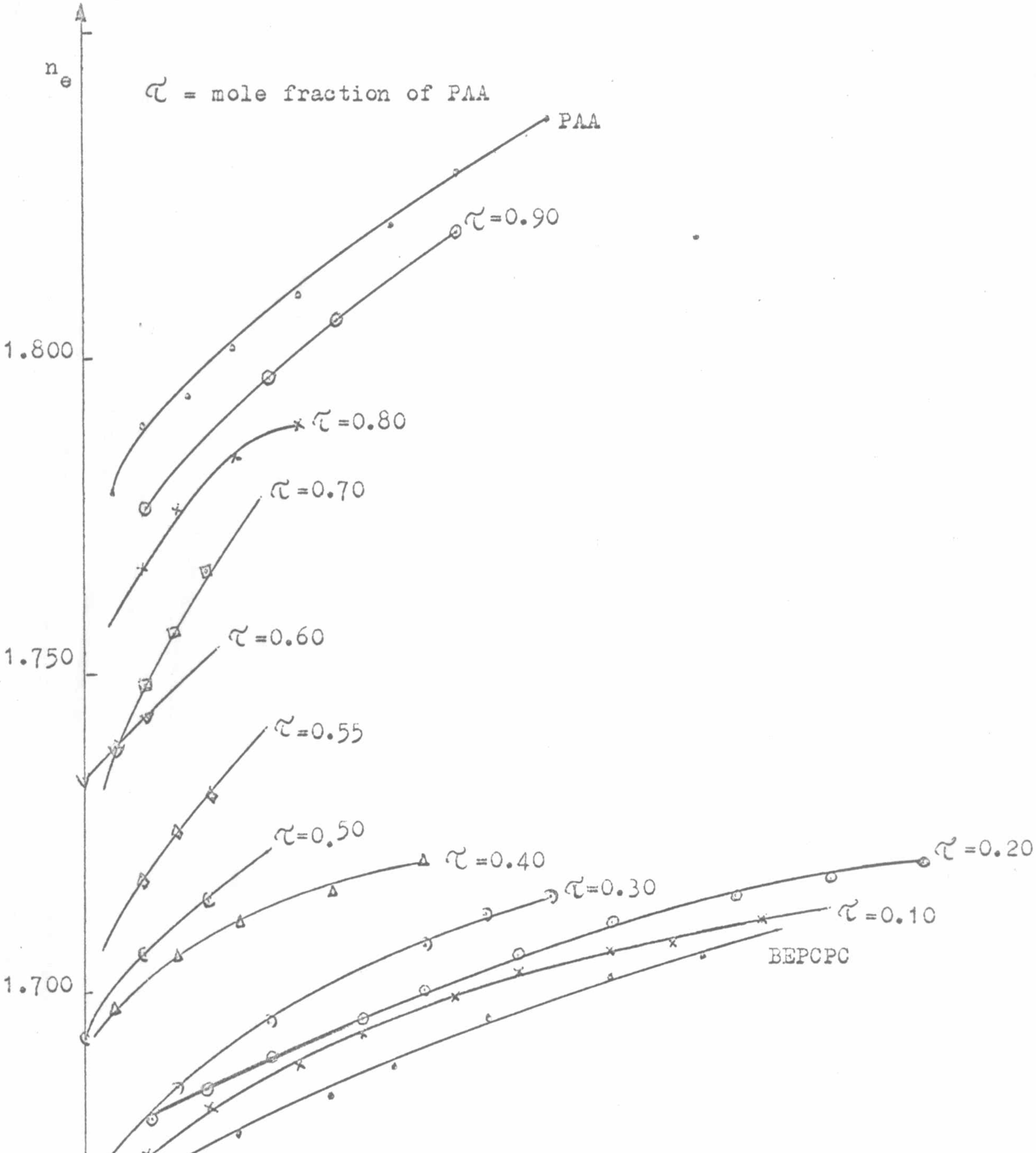

Fig.12 The extraordinary refractive index(n_e) of PAA,BEPCPC and their mixtures plotted against the relative temperature.

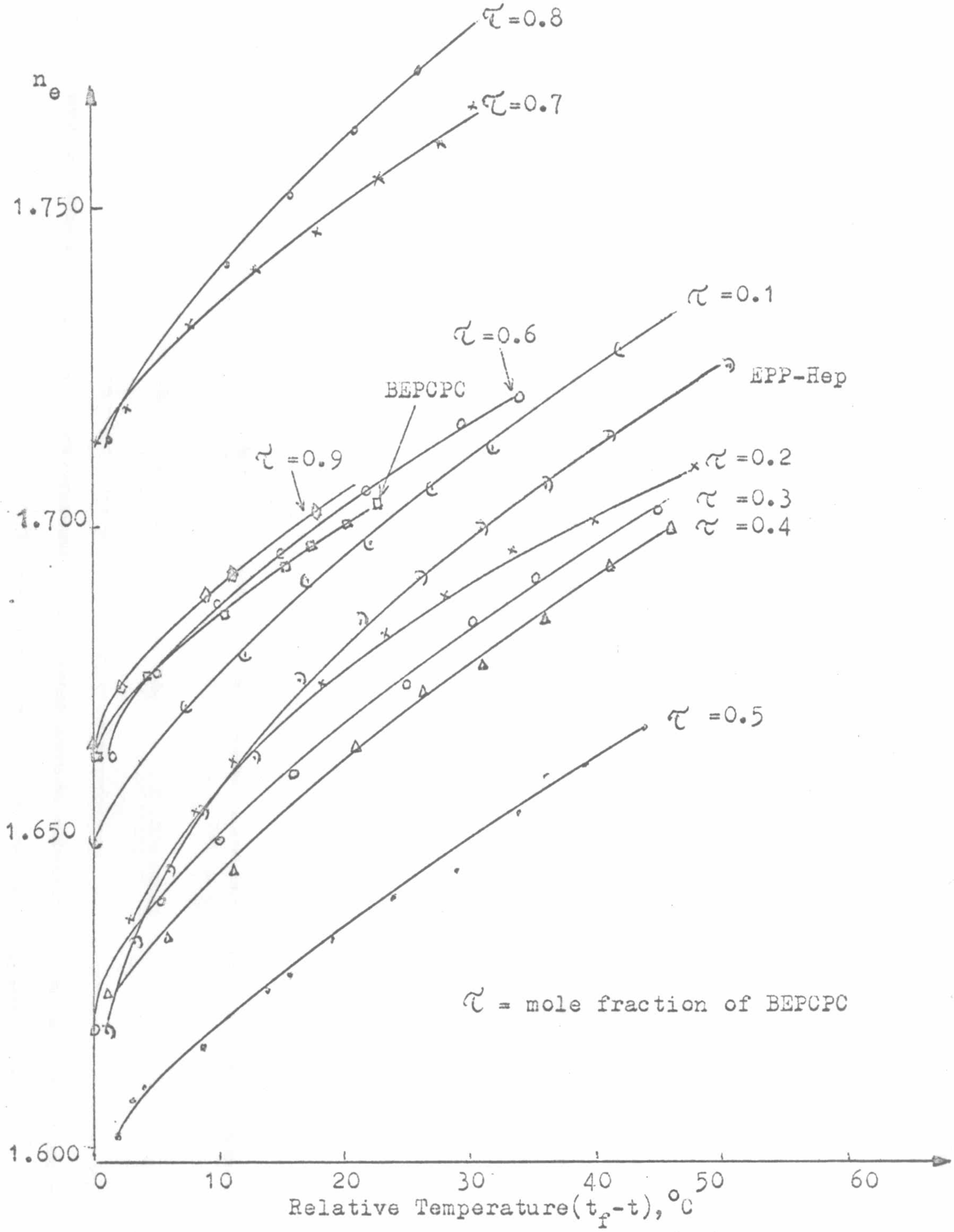

Fig.13 The extraordinary refractive index(n_e) of EPP-Hep, BEPCPC and their mixtures plotted against the relative temperature.

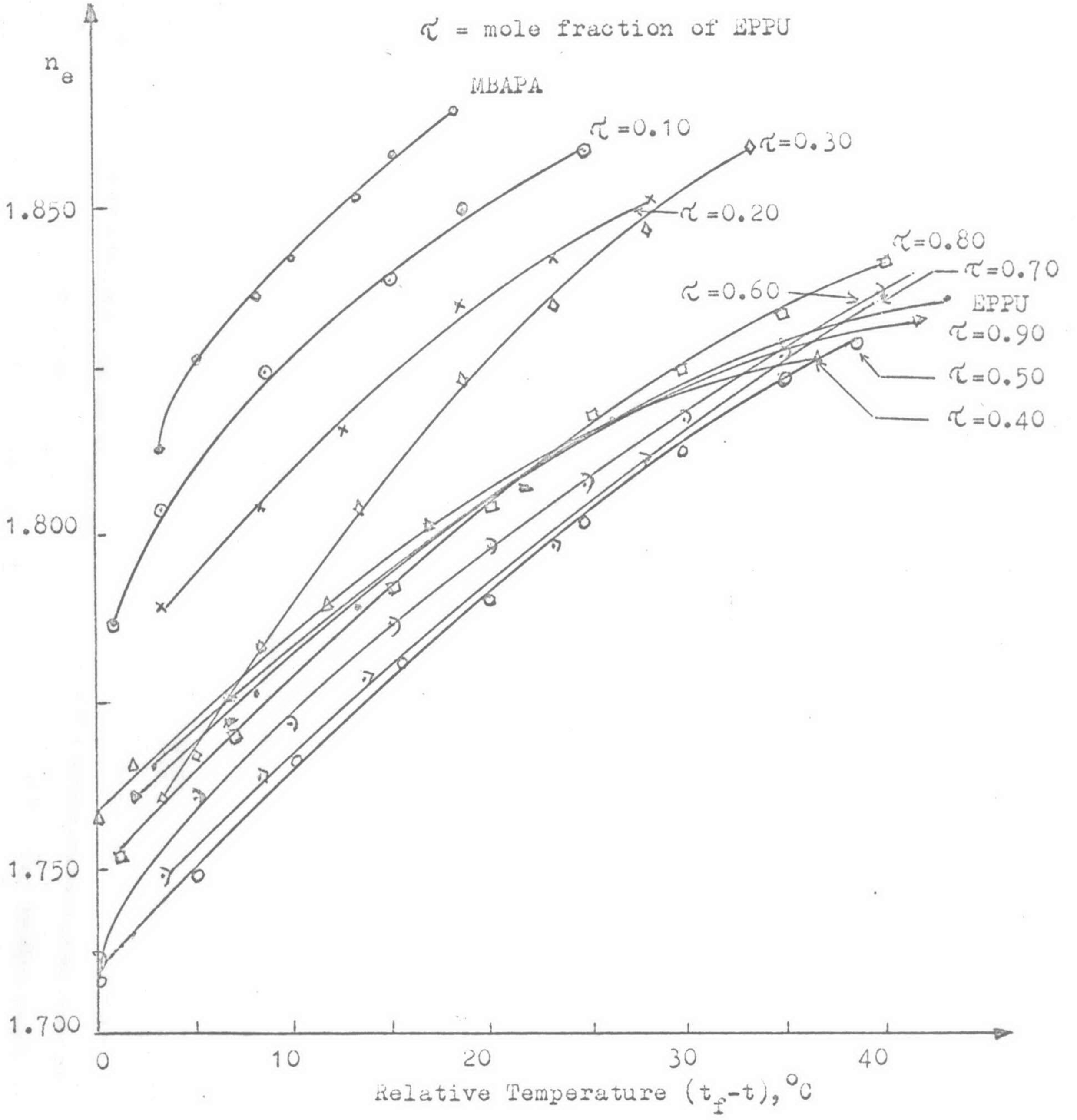

Fig. 14 The extraordinary refractive index (n_e) of EPPU, MBAPA and their mixtures plotted against the relative temperature.

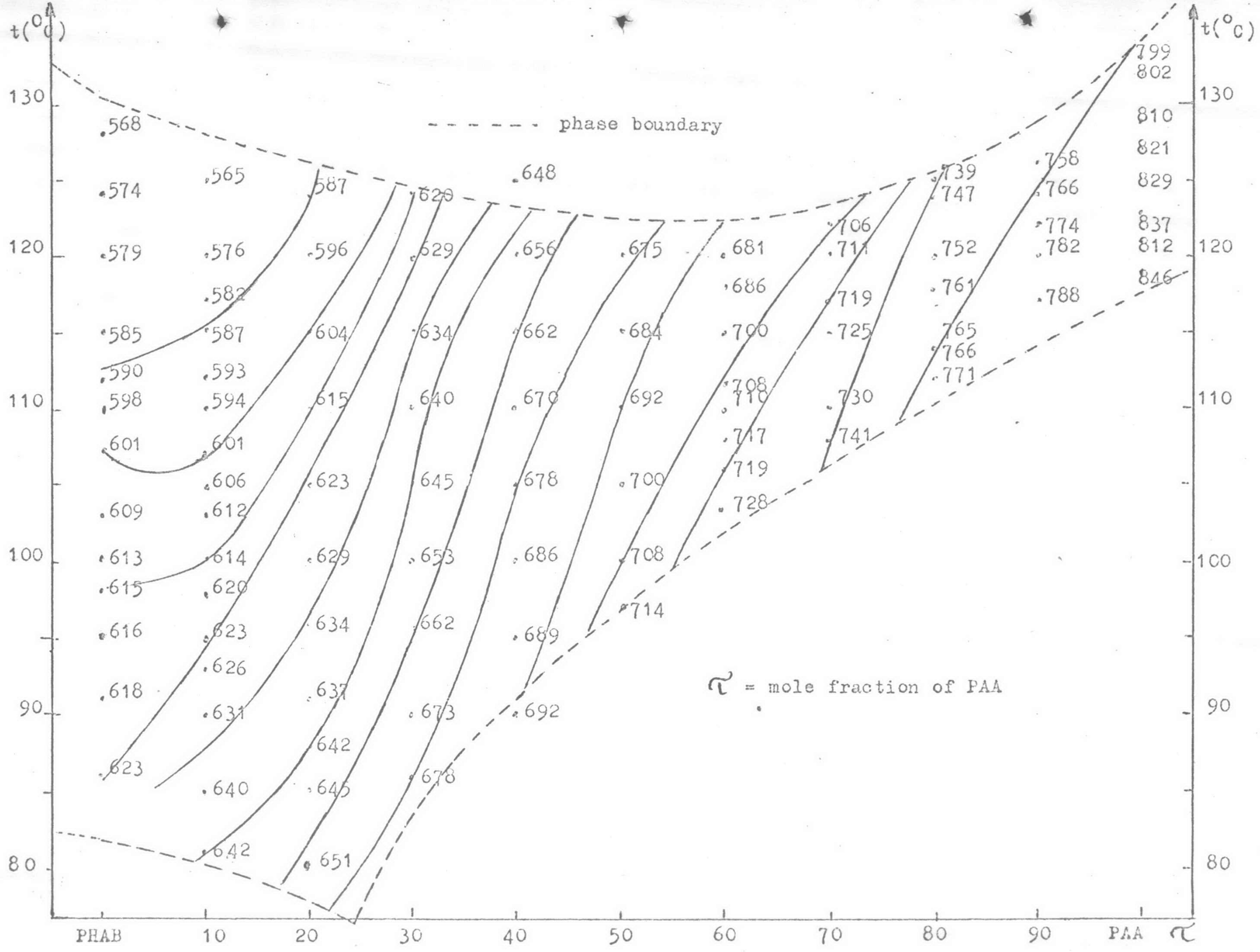

Fig.15 The contours of (n_e-1) in the temperature-composition plane of PAA and PHAB

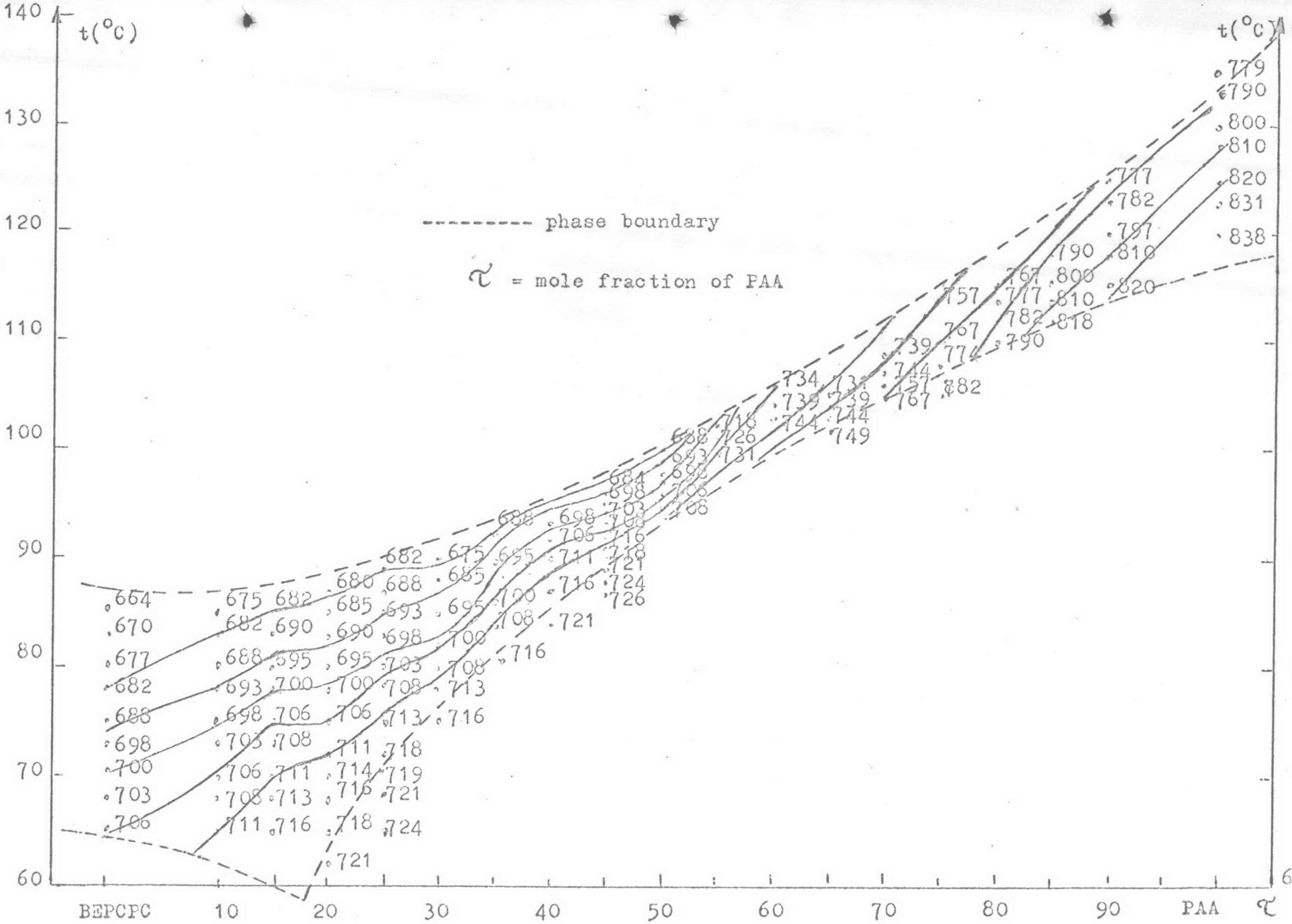

Fig.16 The contours of (n_e-1) in the temperature-composition plane of PAA and BEPCPC

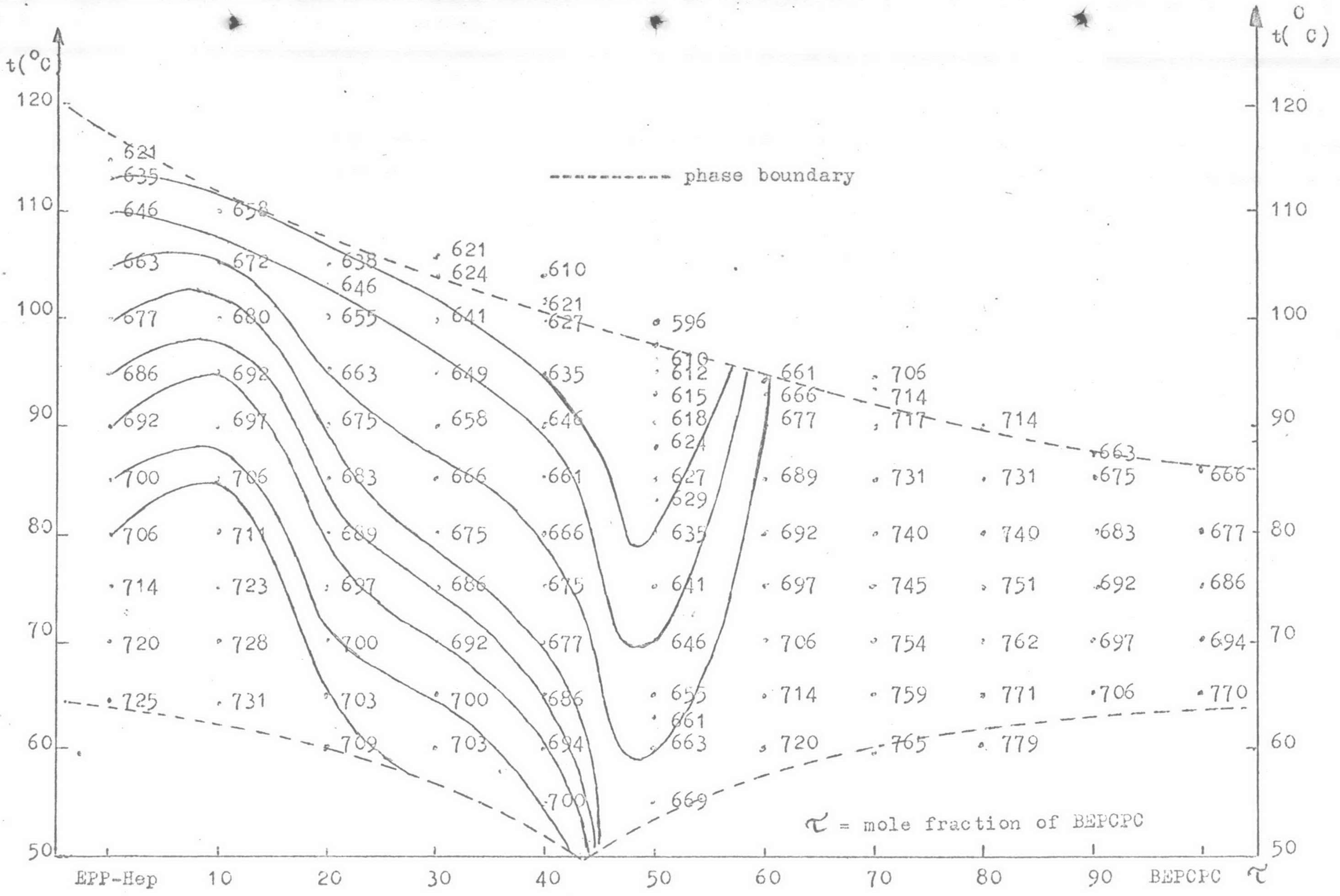

Fig.17 The contours of (n_e-1) in the temperature-composition plane of EPP-Hep and BEPCPC

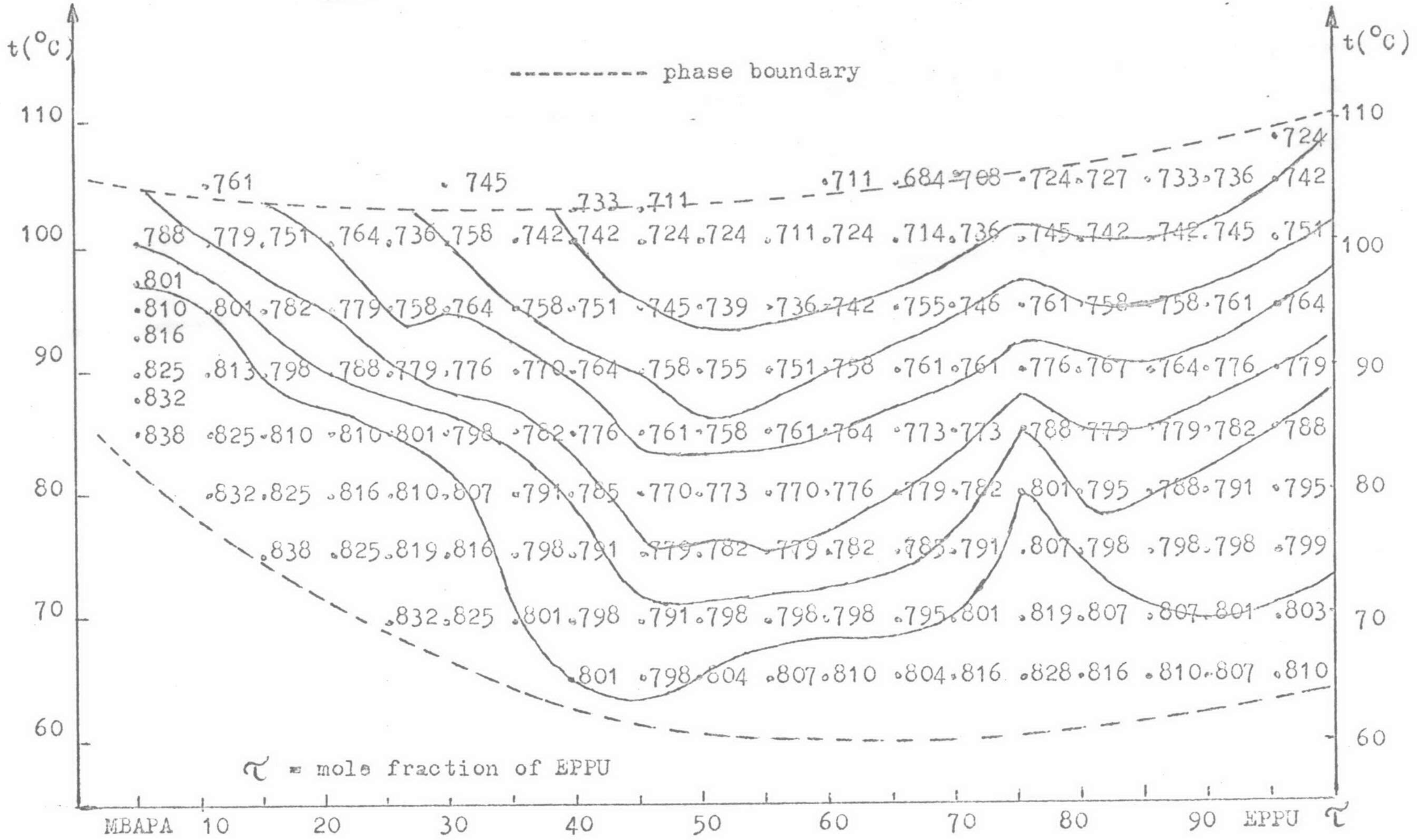

Fig. 18 The contours of $(n_e - 1)$ in the temperature-composition plane of EPPU and MBAPA

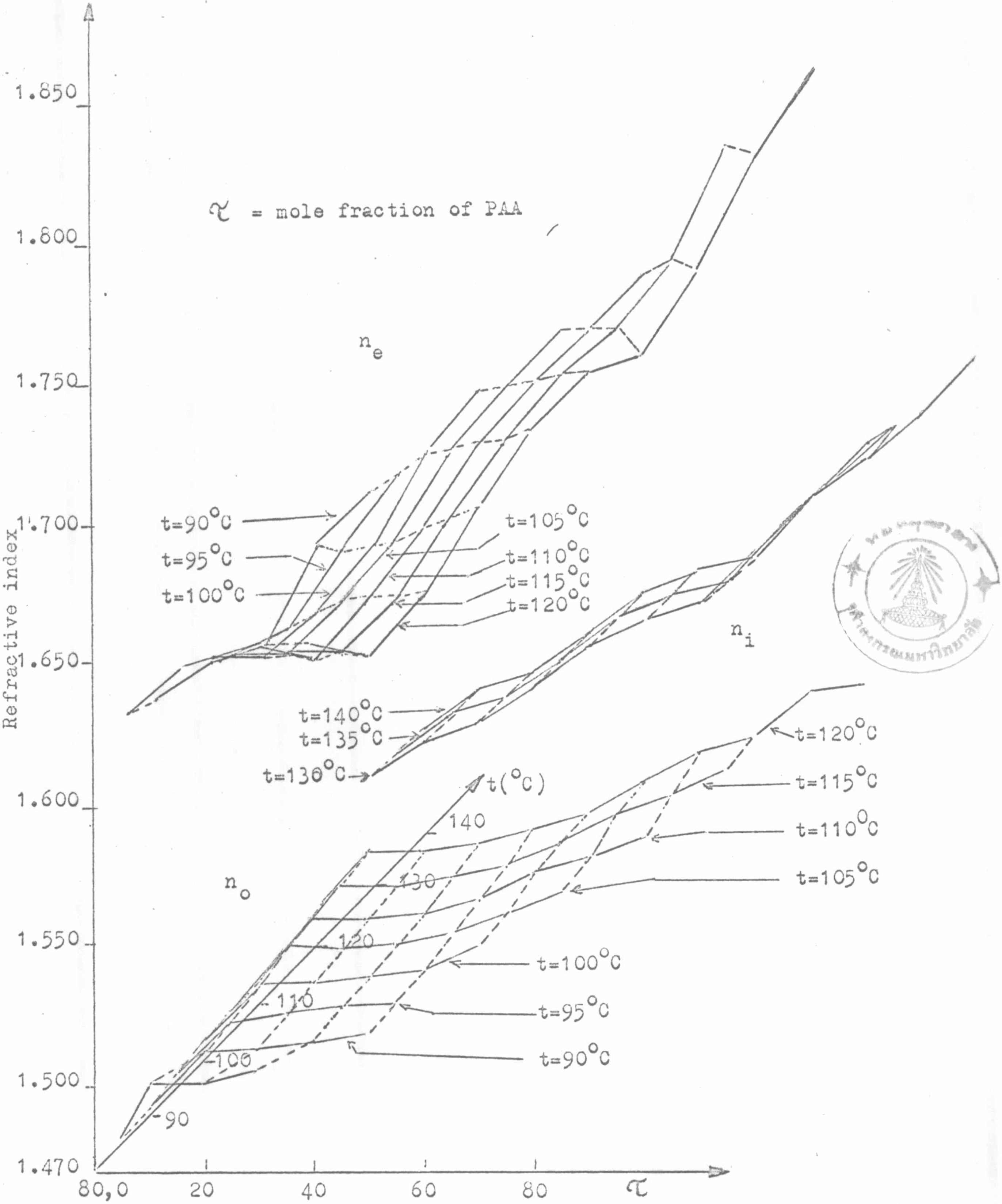

Fig.19 Perspective plots of the refractive indices n_e, n_o, n_i of PAA, PHAB and their mixtures in the temperature-composition plane.

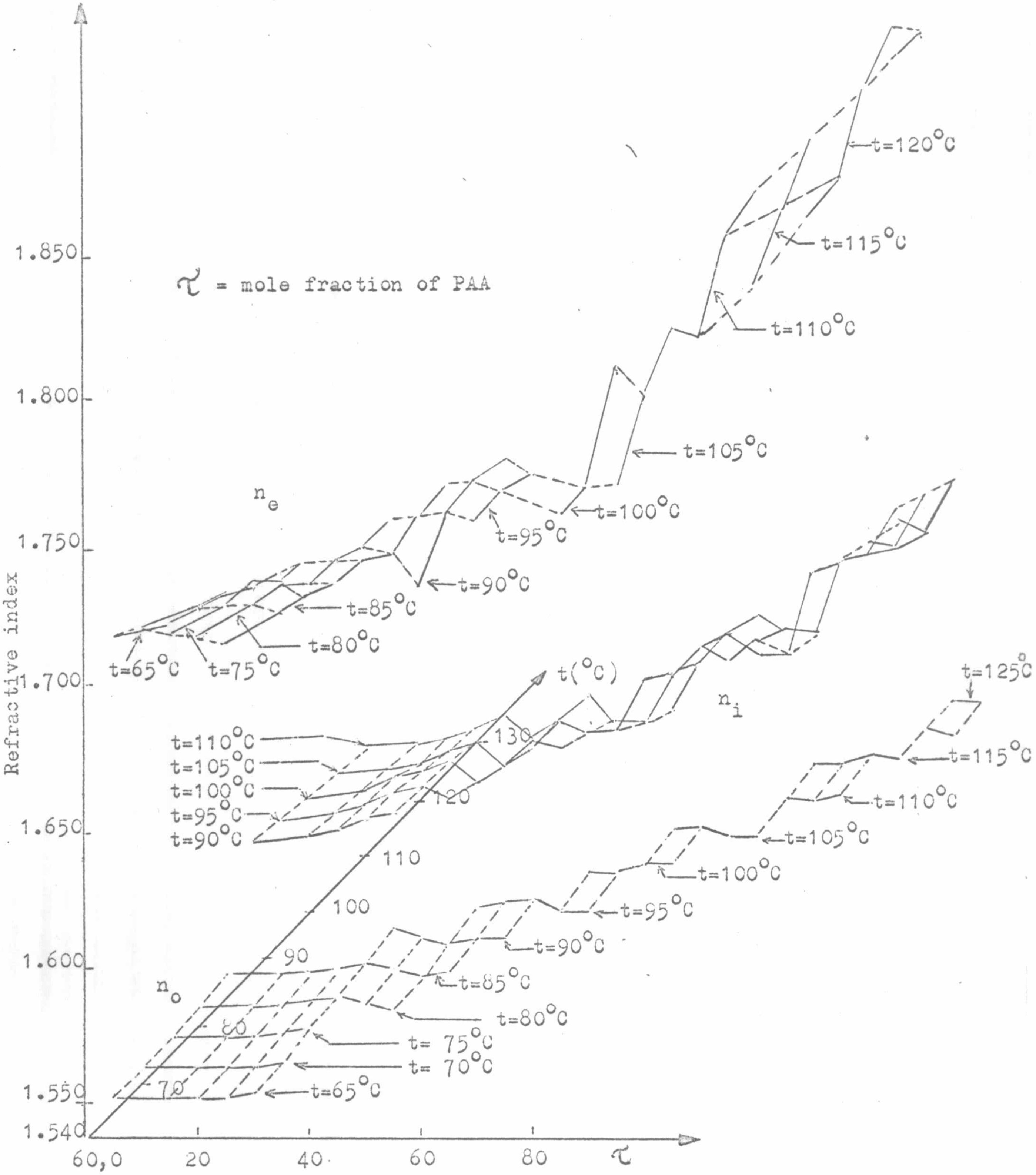

Fig.20 Perspective plots of the refractive indices n_e, n_o, n_i of PAA, BEPCPC and their mixtures in the temperature-composition plane.

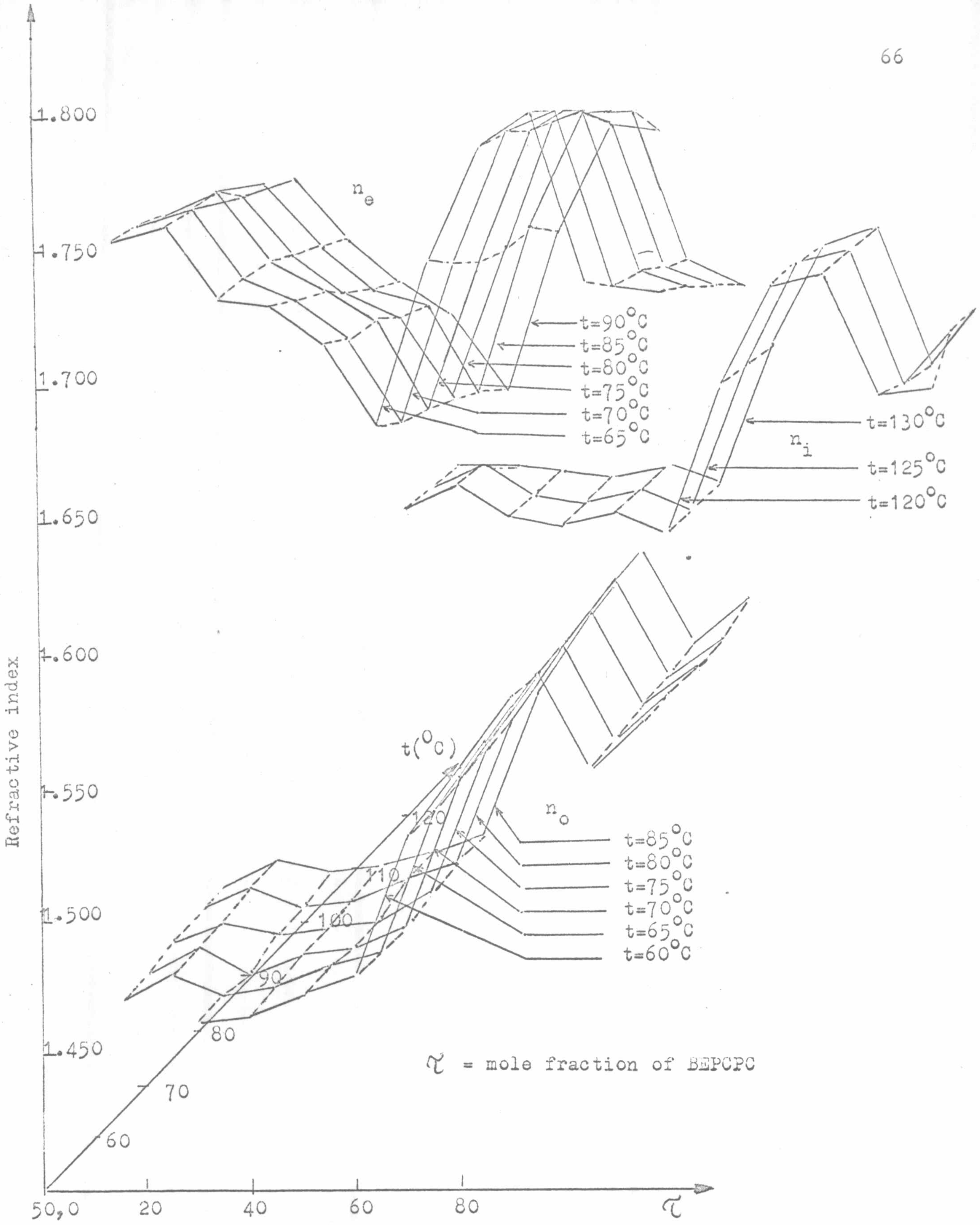

Fig.21 Perspective plots of the refractive indices n_e, n_o, n_i of EPP-Hep, BEPCPC and their mixtures in the temperature-composition plane.

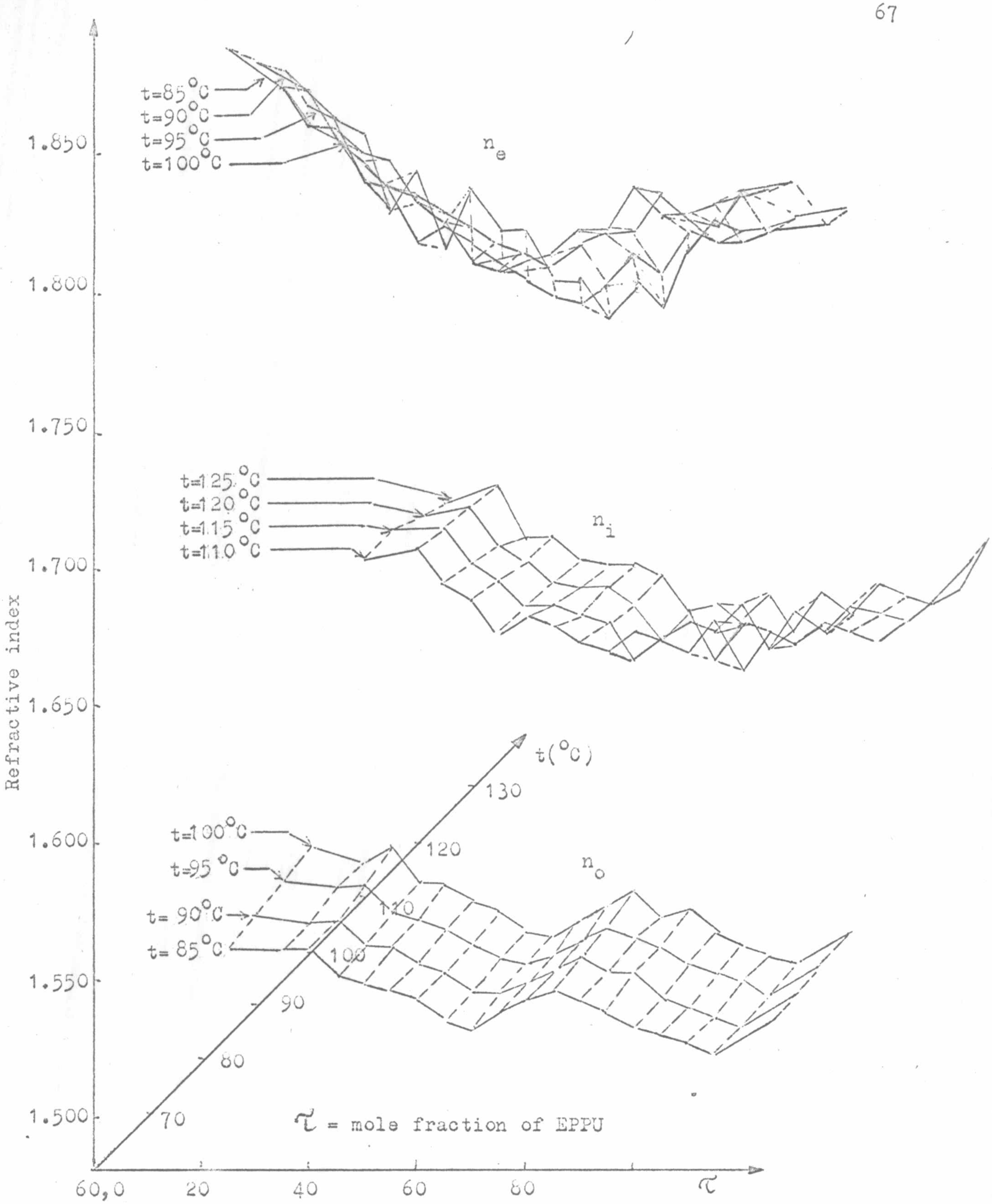

Fig.22 Perspective plots of the refractive indices n_e, n_o, n_i of EPPU, MBAPA and their mixtures in the temperature- composition plane.

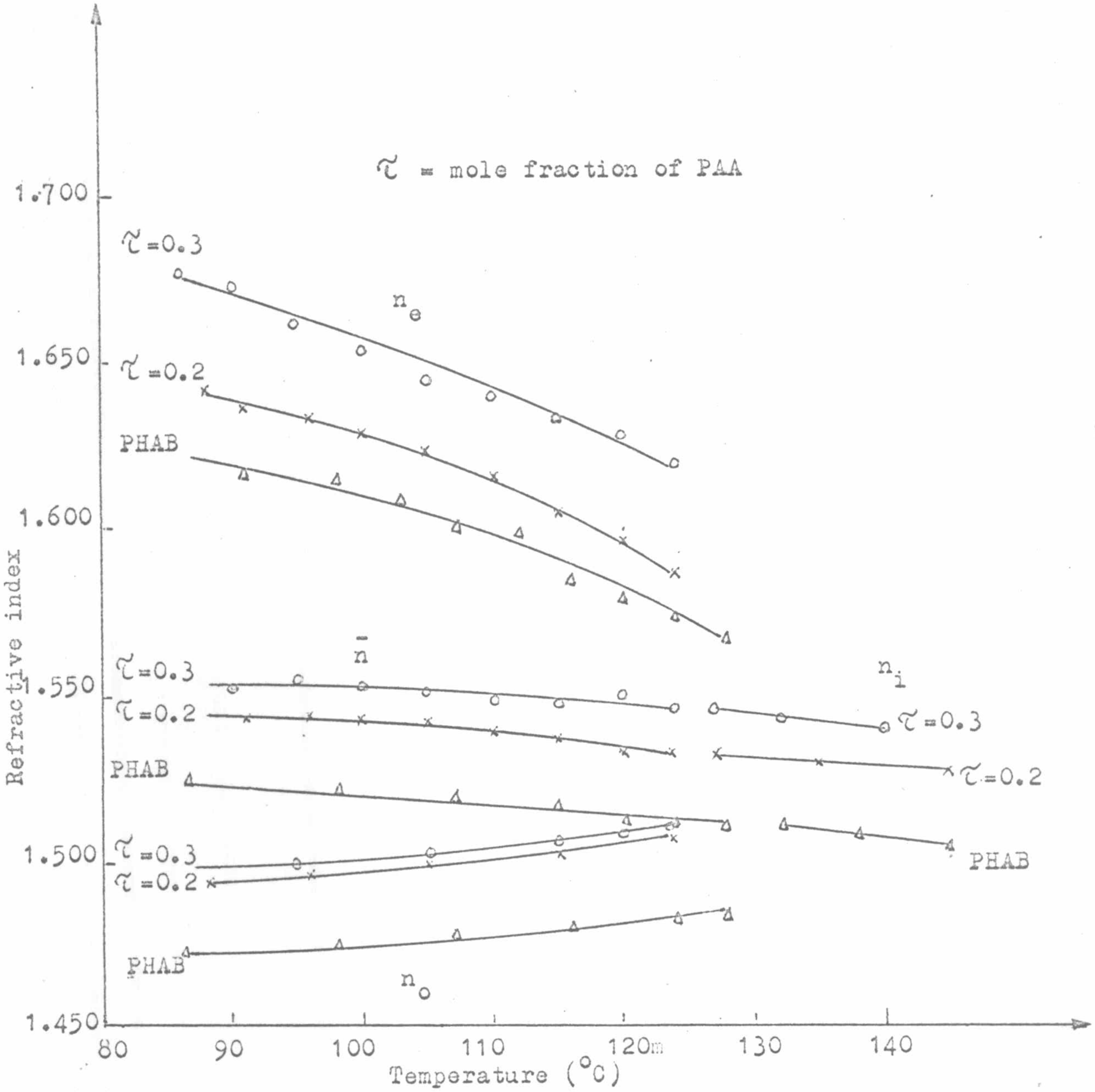

Fig.23 Temperature dependence of the refractive indices of PAA, PHAB and their mixtures.

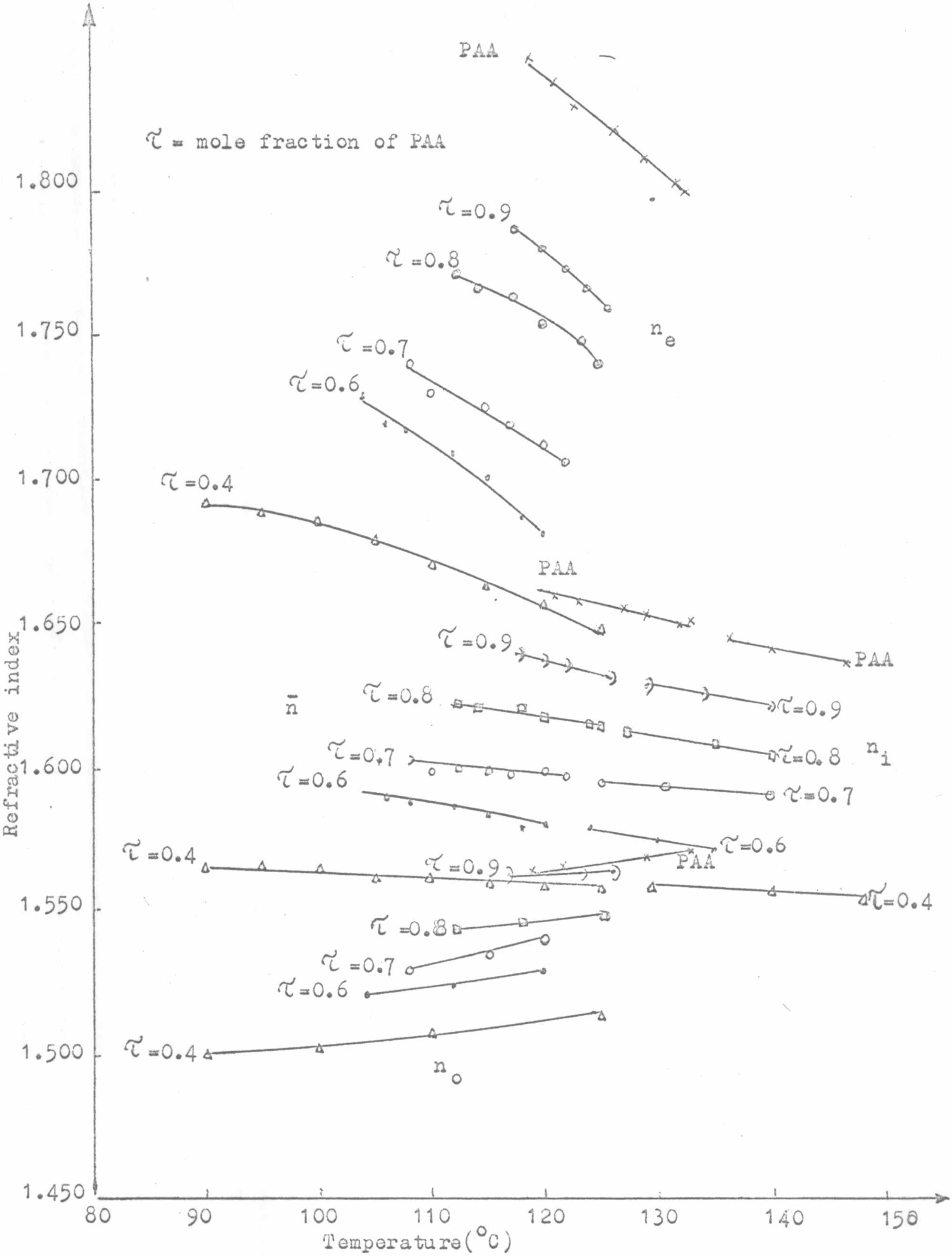

Fig.24 Temperature dependence of the refractive indices of PAA, PHAB and their mixtures.

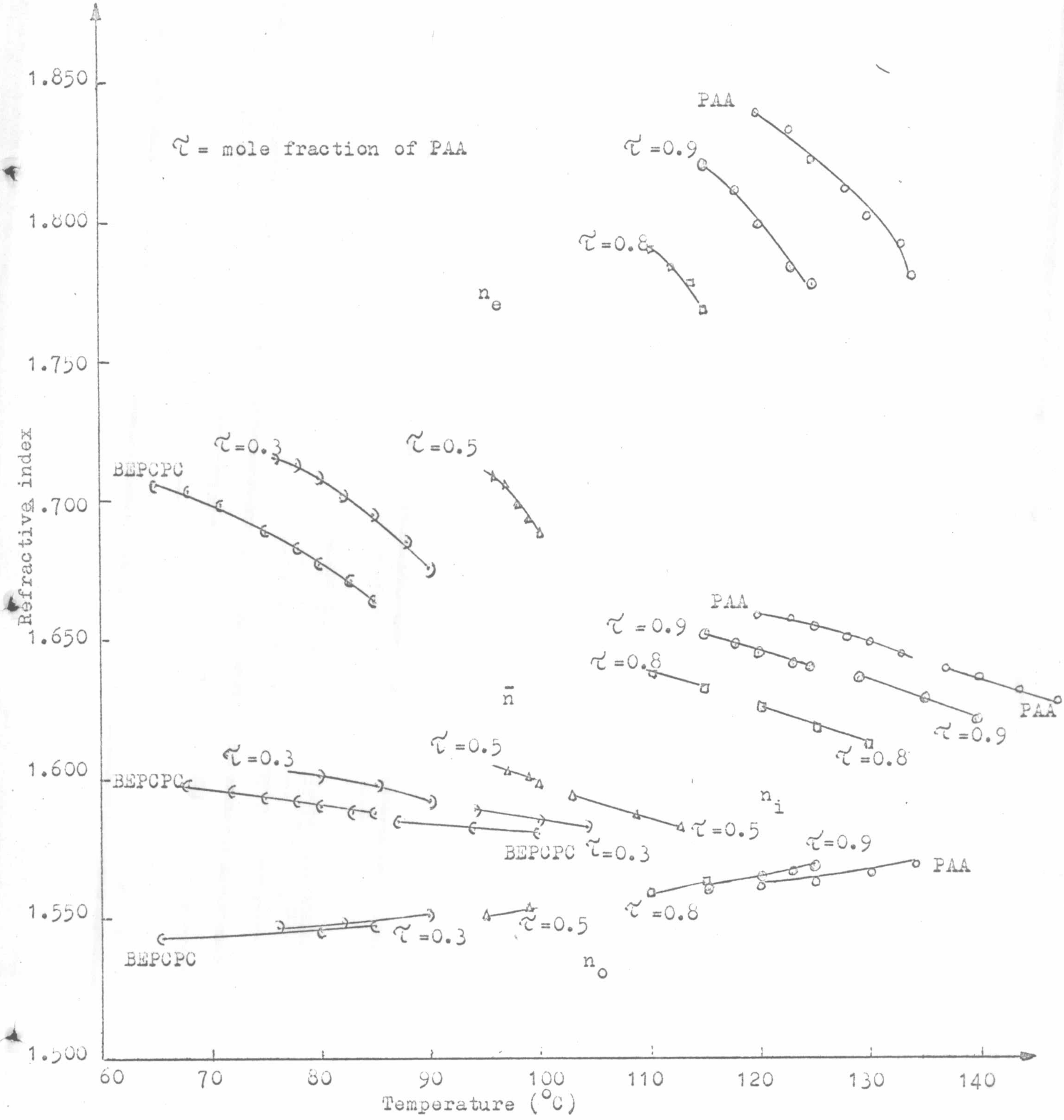

Fig. 25 Temperature dependence of the refractive indices of PAA, BEPCPC and their mixtures.

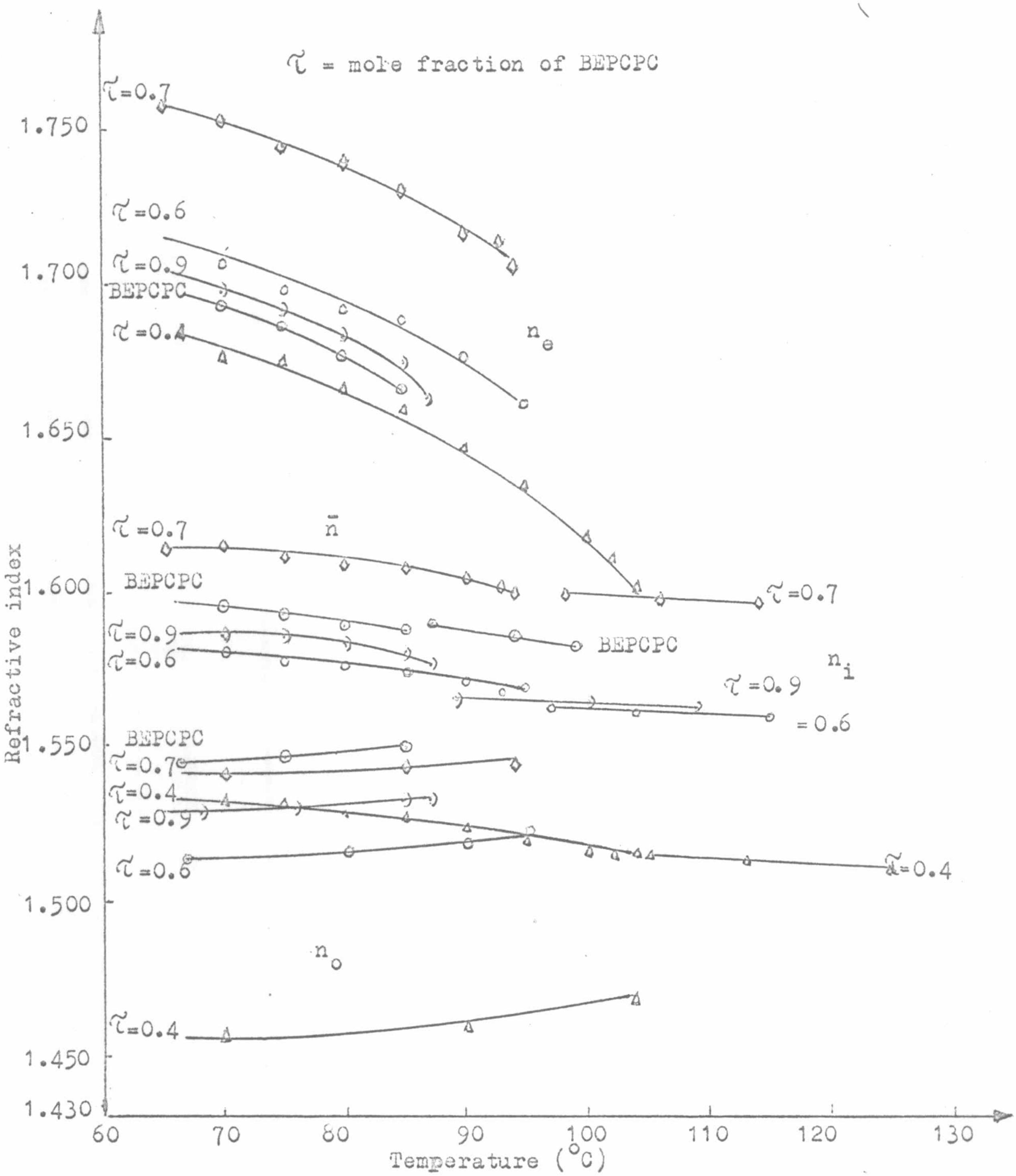

Fig.26 Temperature dependence of the refractive indices of EPP-Hep, BEPCPC and their mixtures.

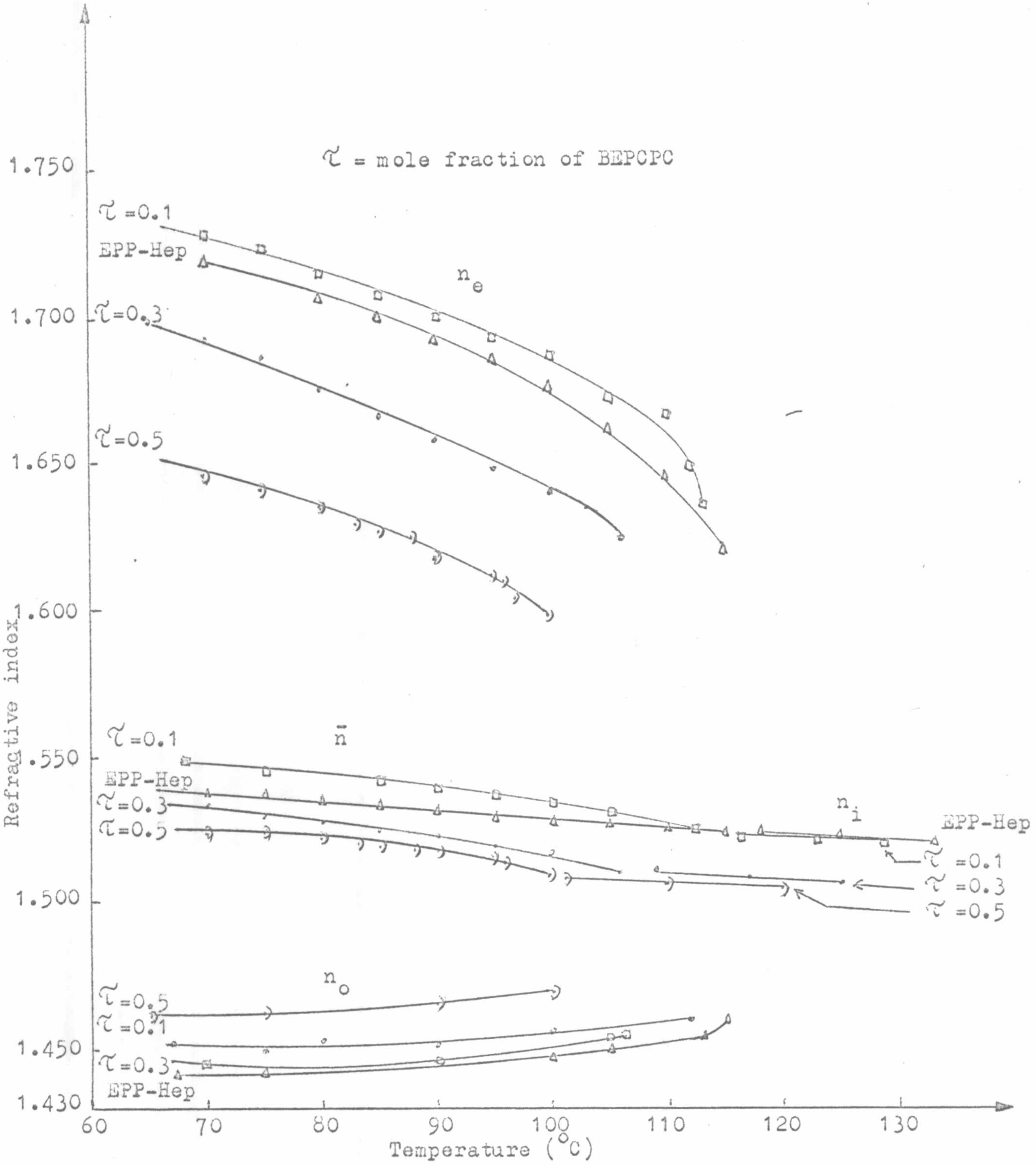

Fig.27 Temperature dependence of the refractive indices of EPP-Hep, BEPCPC and their mixtures.

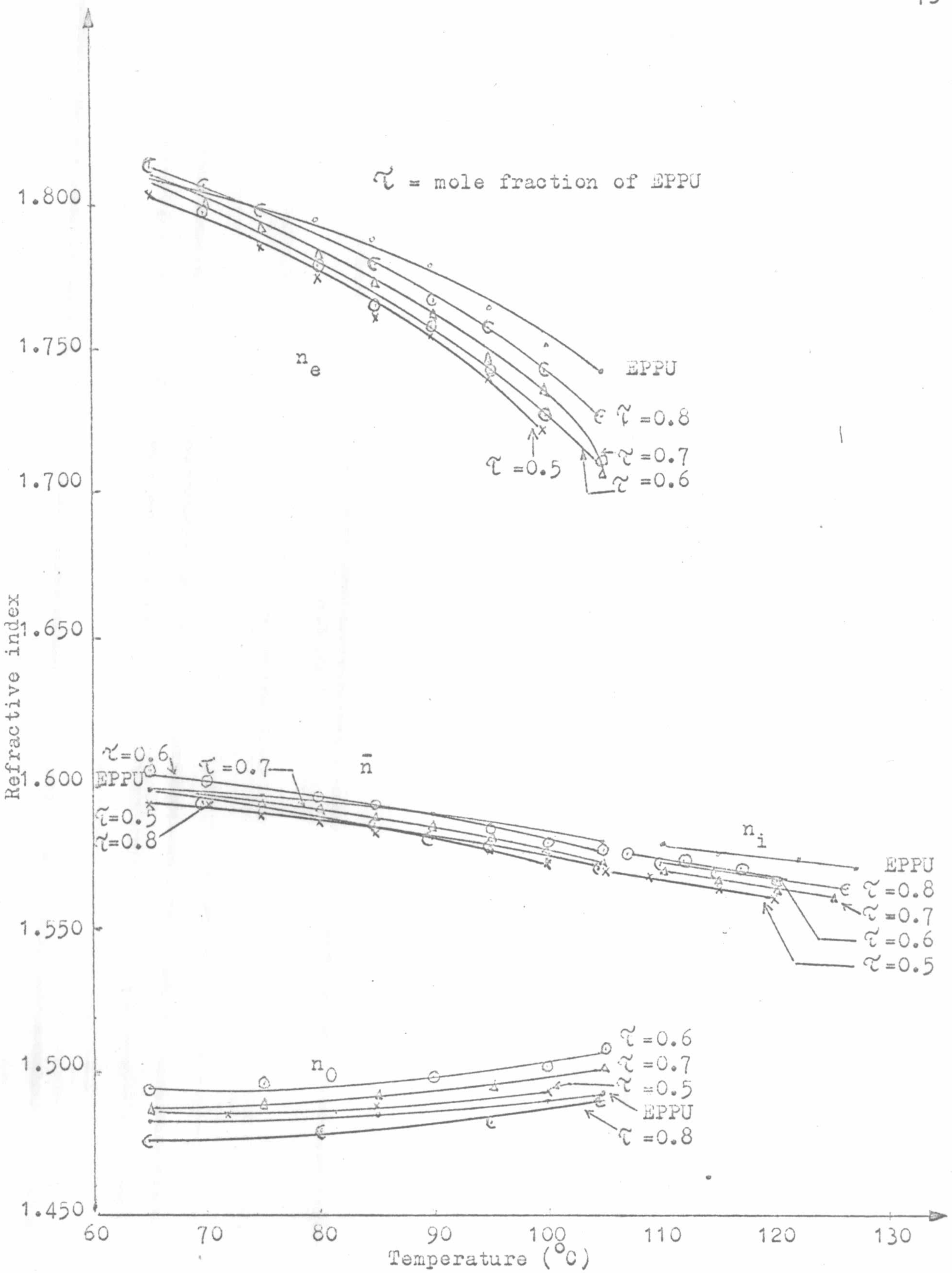

Fig.28 Temperature dependence of the refractive indices of EPPU, MBAPA and their mixtures.

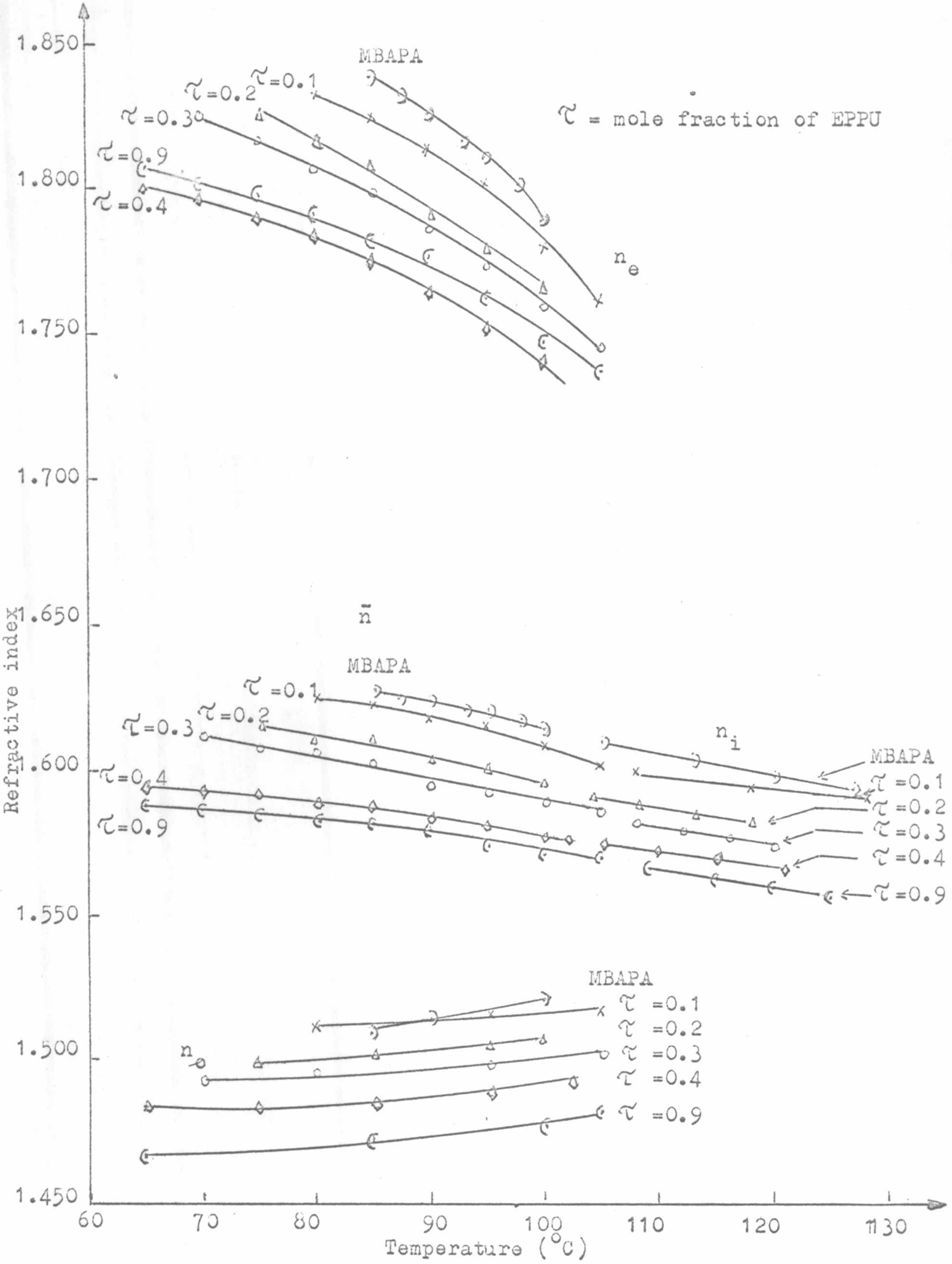

Fig. 29 Temperature dependence of the refractive indices of EPPU, MBAPA and their mixtures.

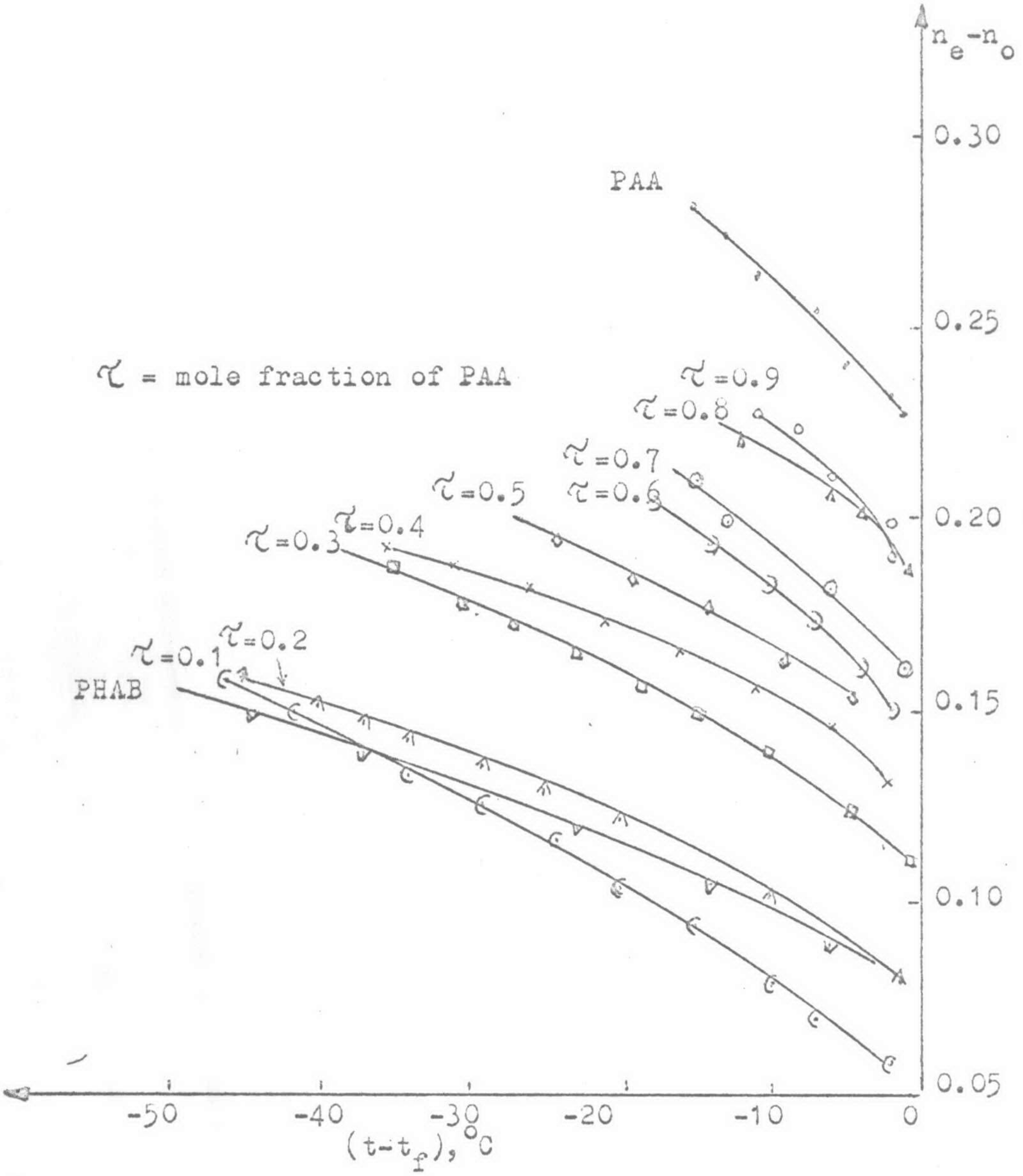

Fig.30 The double refraction of PAA,PHAB and their mixtures plotted against the difference between the temperature of measurement and the transition temperature.

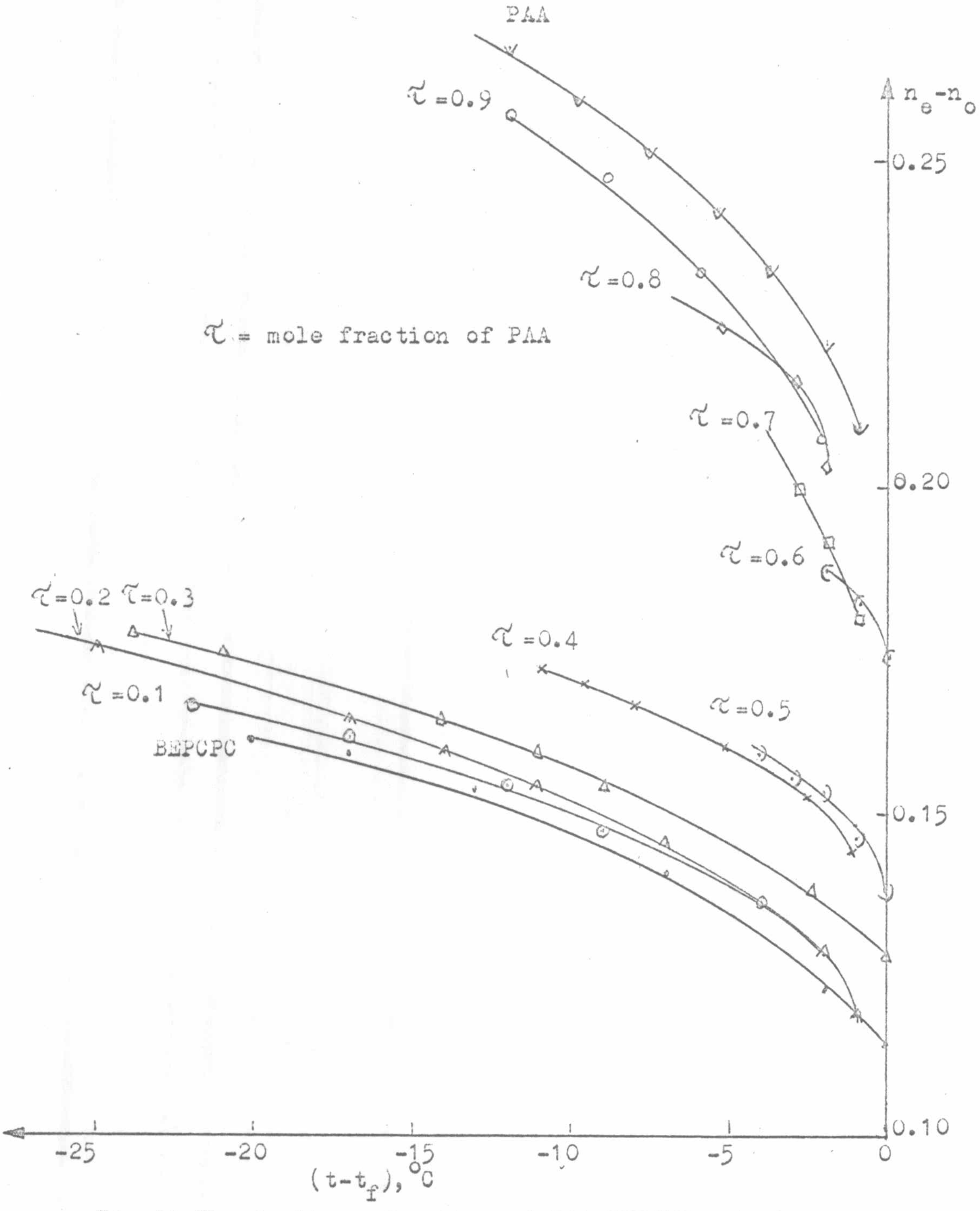

Fig.31 The double refraction of PAA, BEPCPC and their mixtures plotted against the difference between the temperature of measurement and the transition temperature.

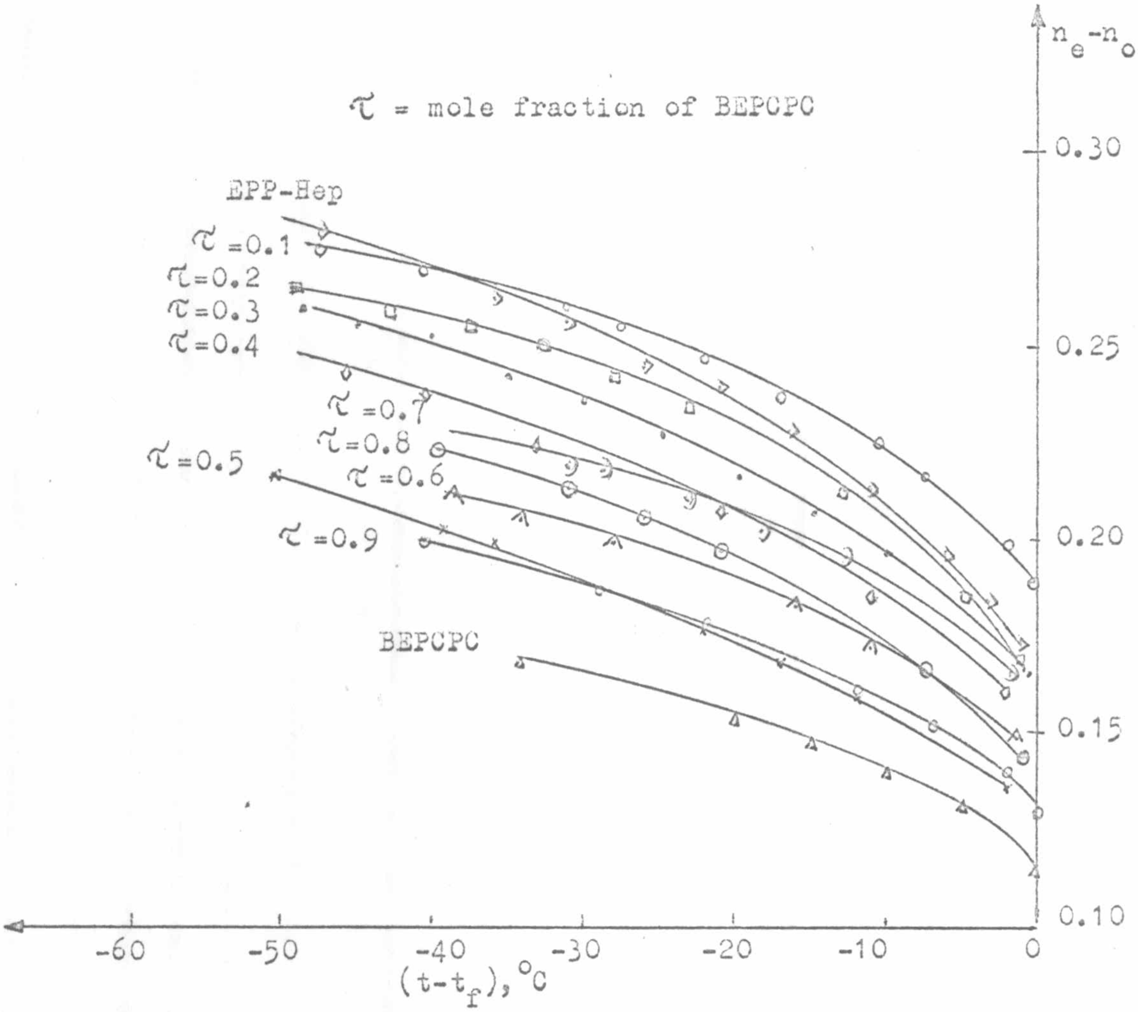

Fig.32 The double refraction of EPP-Hep, BEPCPC and their mixtures plotted against the difference between the temperature of measurement and the transition temperature.

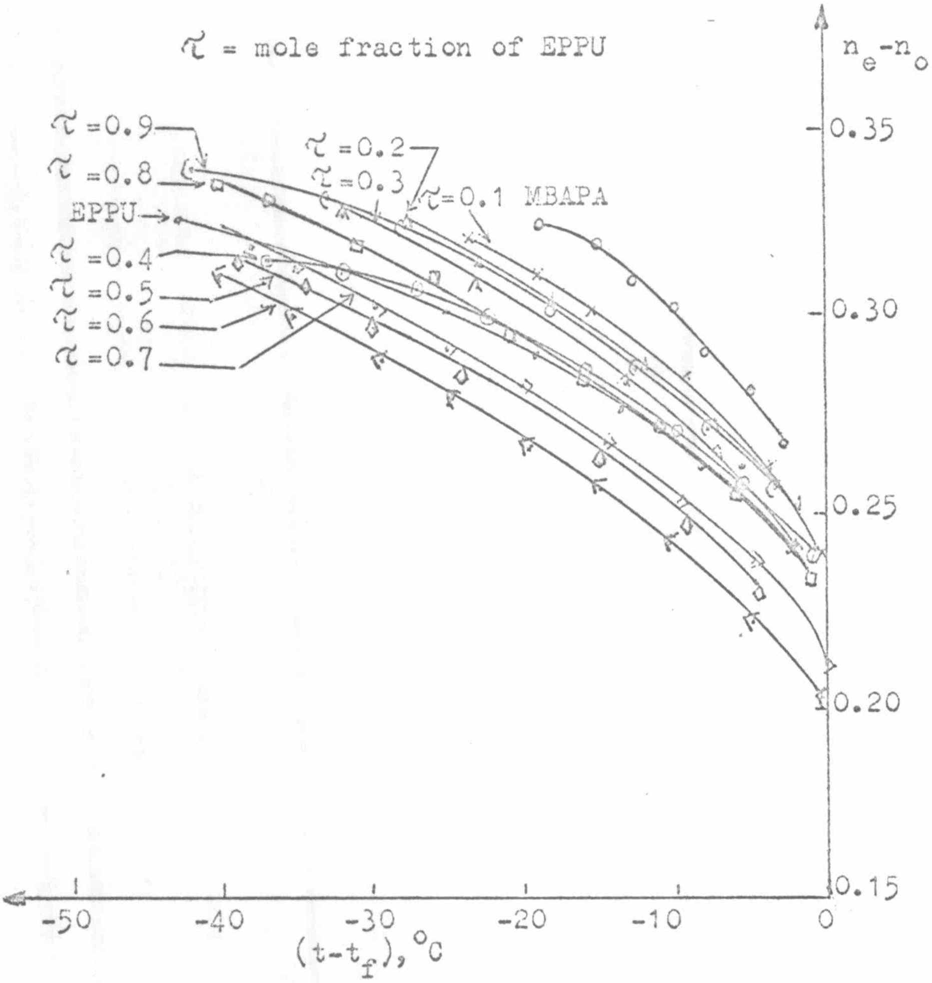

Fig.33 The double refraction of EPPU, MBAPA and their mixtures plotted against the difference between the temperature of measurement and the transition temperature.

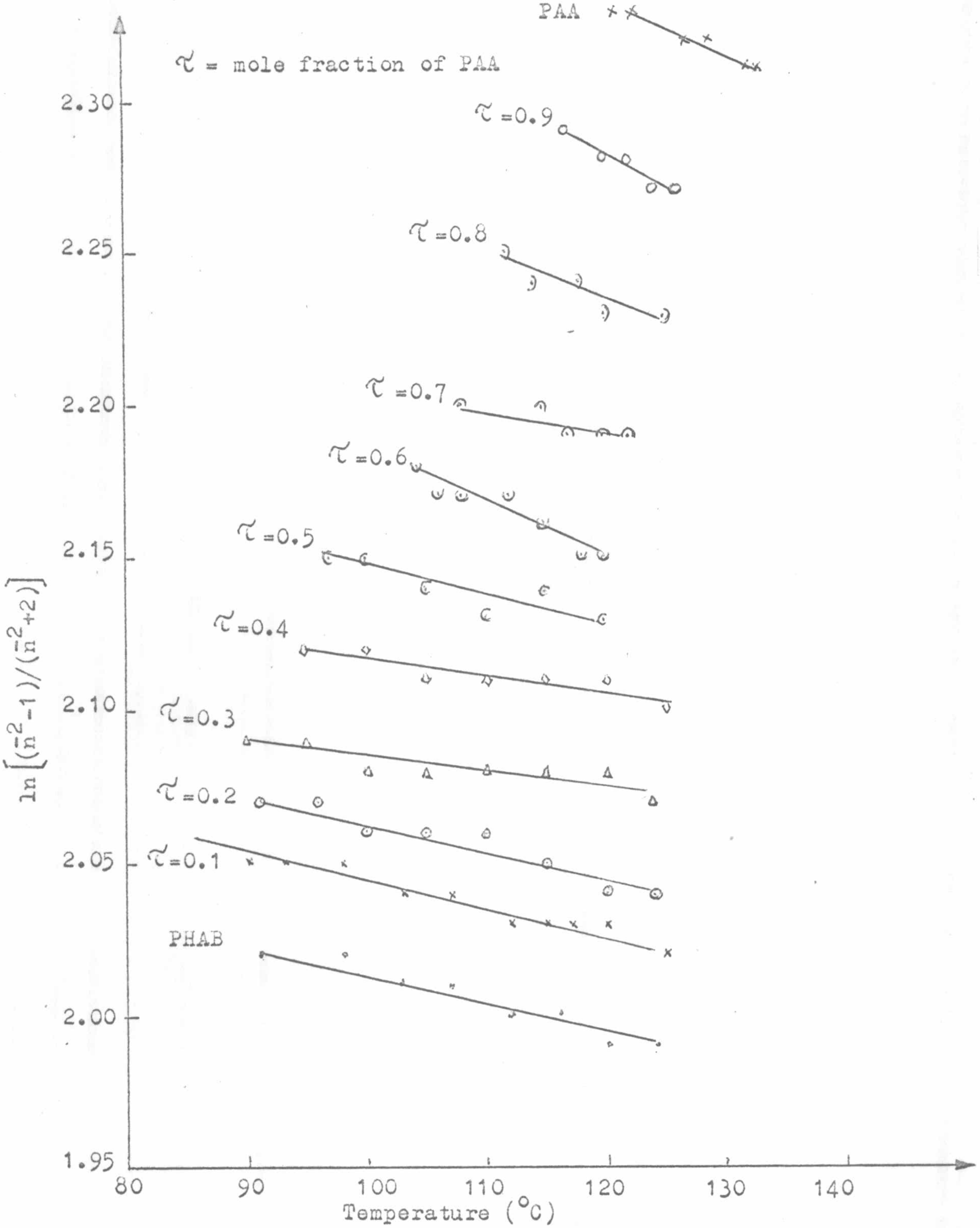

Fig.34 Plots of $\ln\left[(\bar{n}^2-1)/(\bar{n}^2+2)\right]$ versus temperature for PAA, PHAB and their mixtures.

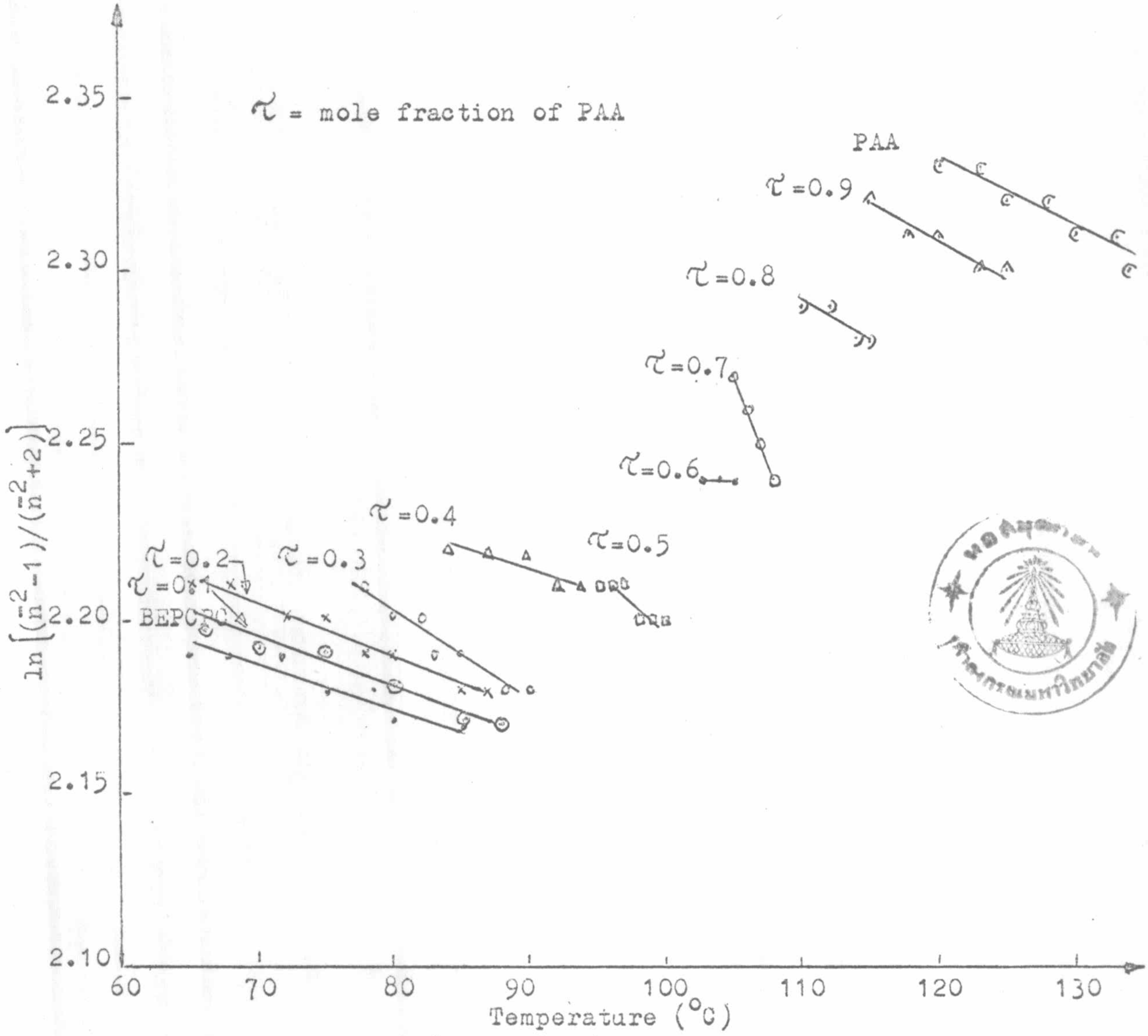

Fig.35 Plots of ln [($\bar{n}^2$-1)/($\bar{n}^2$+2)] versus temperature for PAA, BEPCPC and their mixtures.

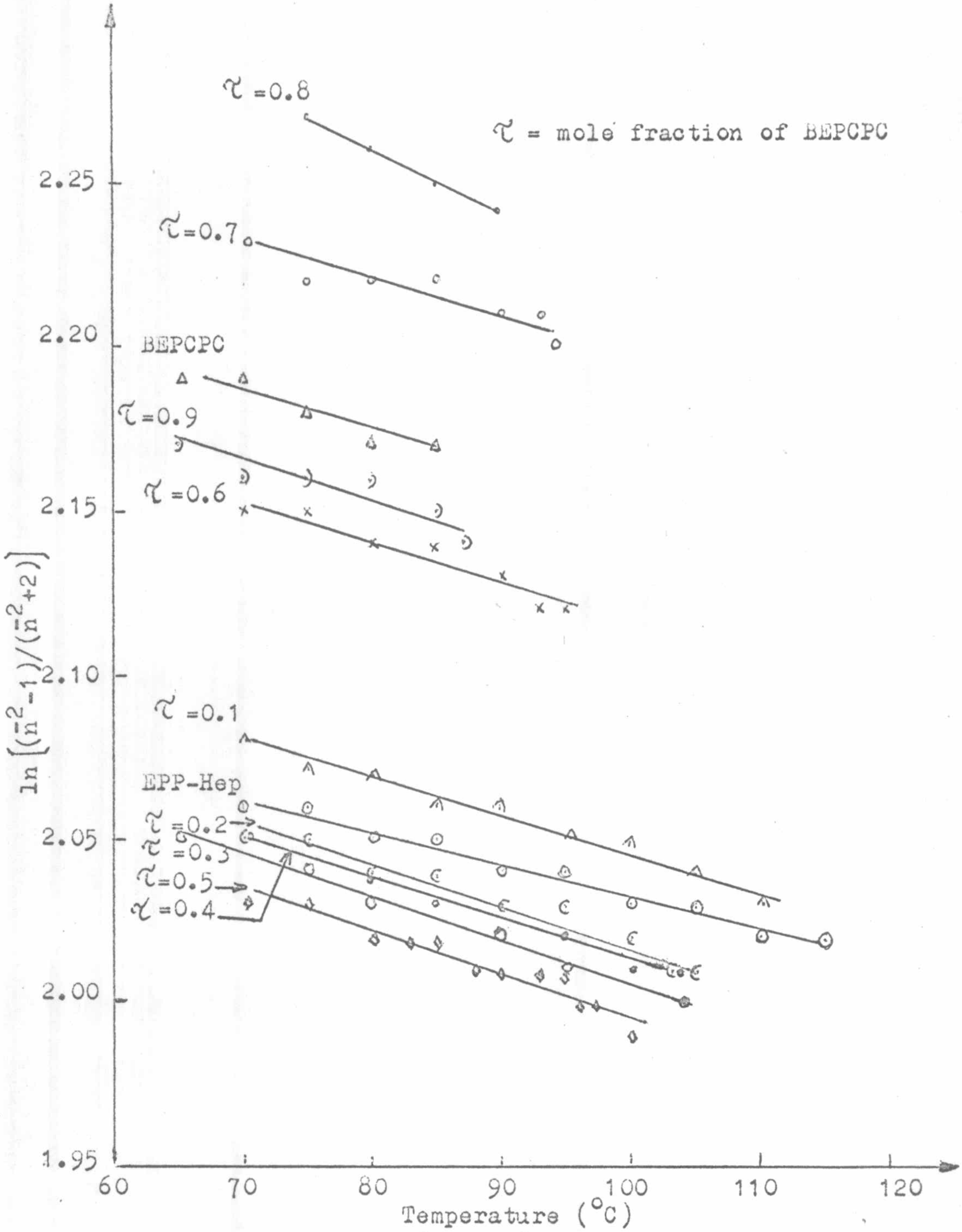

Fig.36 Plots of $\ln\left[(\bar{n}^2-1)/(\bar{n}^2+2)\right]$ versus temperature for EPP-Hep, BEPCPC and their mixtures.

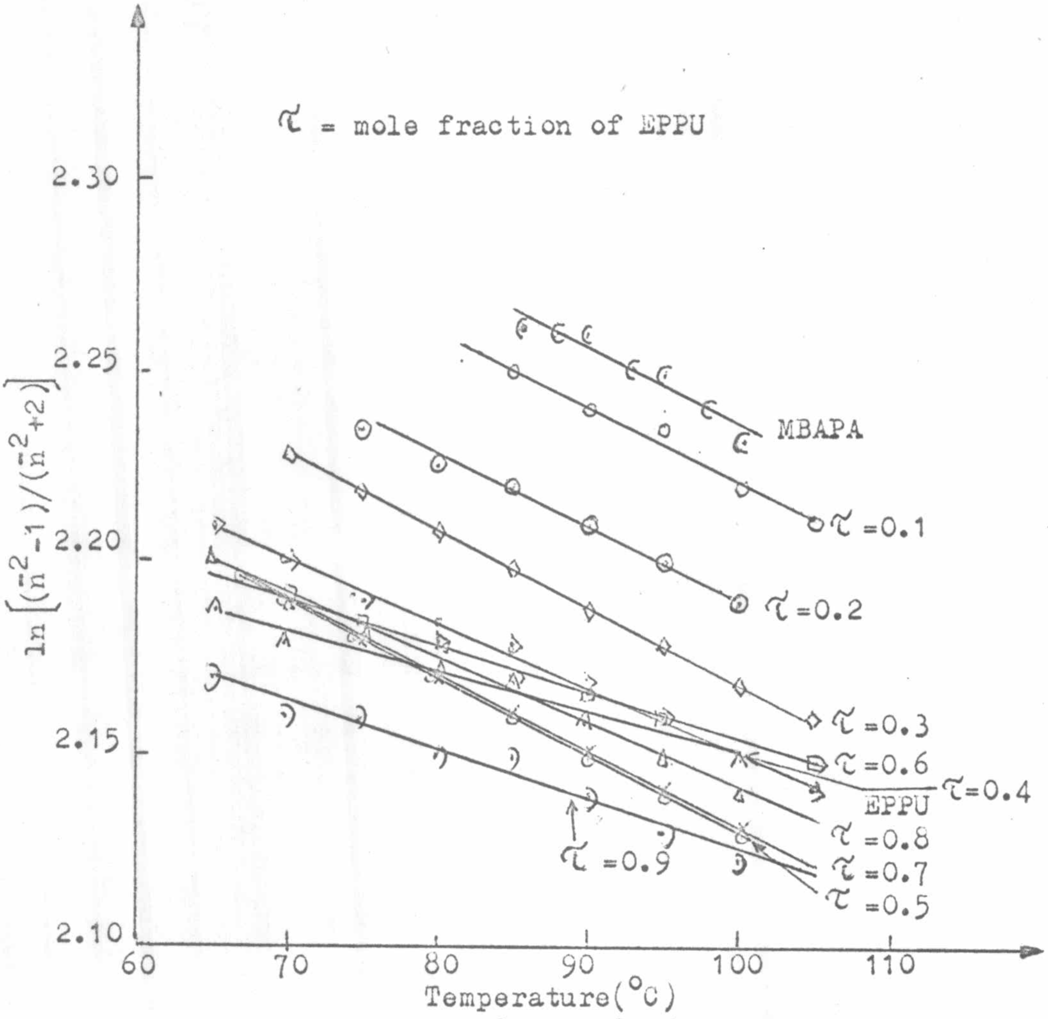

Fig.37 Plots of $\ln\left[(\bar{n}^2-1)/(\bar{n}^2+2)\right]$ versus temperature for EPPU, MBAPA and their mixtures.