

Optical Rotatory Dispersion and Ultraviolet Spectrum Studies of Poly[(+)-2-methylbutyl methacrylate] and Monomeric Analogue

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ABSTRACT: ORD and UV measurements were carried out on poly[(+)-2-methylbutyl methacrylate]s (PMBMA) with various tacticities and on the monomeric analogue.

Specific rotation ($[\alpha]$, measured between 400 and 250 $m\mu$) of isotactic (*i*-) PMBMA is larger and that of atactic (*a*-)PMBMA is smaller than that of the monomeric analogue at room temperature. Extinction coefficient (k , measured at 217 $m\mu$) of *i*-PMBMA is larger than that of *a*-PMBMA. The monomeric analogue showed the lowest absorption.

Specific rotation of *i*-PMBMA and the monomeric analogue decreases, while that of *a*-PMBMA increases with increasing temperature. Values of the temperature coefficient of $[\alpha]$, $\Delta[\alpha]/[\alpha]\Delta T$, of these three samples are of the order of 10^{-3} . In the case of *n*-heptane and dioxane solutions, the absolute value of $\Delta[\alpha]/[\alpha]\Delta T$ of each sample measured between 60 and 70°C is smaller than that obtained between 50 and 60°C.

The extinction coefficient of these samples decreases with temperature and the relative temperature effects of k , $\Delta k/k\Delta T$, are of the order of 10^{-3} . The absolute value of $\Delta k/k\Delta T$ of *i*-PMBMA is greater, but that of *a*-PMBMA and the monomeric analogue is smaller in the high temperature range (60 to 70°C) than in the low temperature range (30 to 40°C).

The significant differences observed in a series of optical behavior may arise from the differences in the electronic perturbation of chromophores originating from conformational differences (including the conformation of -COO groups) in the very local parts of the polymer chain.

KEY WORDS Poly[(+)-2-methylbutyl methacrylate] / Poly(methyl methacrylate)/ORD/UV/Stereoregularity/Temperature Dependence/Local Conformation /

It is well known that the measurement of optical activity is a useful method for the determination of the conformational correlation between the repeating units along the polymer chain. The ultraviolet (UV) spectrum is also considered to reflect the local structure of the polymer chain.

To date, syntheses of various optically active polymethacrylic esters, *e. g.*, poly[(+)-1, 3-dimethylbutyl]^{1,6} poly[(*l/d*)-bornyl]^{2,7} poly[(*l*-menthyl,^{3,5,7,8} poly[(+)-2-methylbutyl]⁴ and poly[(*l/d*)- α -methylbenzyl]^{8,9} methacrylate]s, have been carried out and their optical activity was investigated in connection with stereoregularity,^{3,9} the position of the asymmetric carbon atoms and the stereostructures of optically active side groups. Differences in optical rotatory power observed

between polymers having varying stereoregularities, and differences between the optical activities of polymers and of the monomeric analogue were attributed to the conformational differences between them. In some cases, a Cotton peak was observed in each optical rotatory dispersion (ORD) curve.^{4,6}

However, a weak point in these studies is the lack of investigation into the temperature dependence of optical activity which is considered to reflect the conformational variations of polymer chains.

Liquori, *et al.*, studied the UV spectra of poly(methyl methacrylate) (PMMA) and found that the extinction coefficient of isotactic PMMA is greater than that of syndiotactic one and decreases with increasing temperature. They also

found a discontinuity at 43°C in the temperature variation of the ratio between the integrals (within 207 and 230 m μ) of the absorbance of isotactic and syndiotactic polymers.¹⁰ However, Ullman, *et al.*, reported that the temperature dependence of the extinction coefficient of poly(*l*-menthyl methacrylate) was very small.⁸

In this paper, ORD and UV spectra, and in particular their temperature dependence, of poly[(+)-2-methylbutyl methacrylate]s (PMBMA) prepared by radical and anionic polymerization processes, and of (+)-2-methylbutyl pivalate (monomeric analogue) are presented. The latter, however, have not yet been investigated in detail. For the purpose of comparison, UV studies of PMMA were carried out.

In order to study structural aspects of the polymers, IR, and NMR results are also presented.

EXPERIMENTAL

Purification of Materials

Methacrylic acid and solvents (toluene, benzene, and others) were purified by ordinary methods, and freshly distilled before use in most cases. Pivalic acid was recrystallized. Commercial (–)-2-methylbutyl alcohol was distilled twice using a 30-cm Vigreux type column, bp 128.5°C and $[\alpha]_D^{25} -4.85$ (optical purity 96%). Other reagents were obtained as "Guaranteed" reagents and used as received.

(+)-2-Methylbutyl Methacrylate (Monomer)

(+)-2-Methylbutyl methacrylate was prepared from methacrylic acid and (–)-2-methylbutyl alcohol in the presence of concd sulphuric acid and hydroquinone: bp 48°C (4.5 mm); yield 95%; $[\alpha]_D^{25} 3.81$ (optical purity was 92%). *Anal.* Found: C, 69.3, H, 10.6%; Calcd: C 69.3, H, 10.4.

(+)-2-Methylbutyl Pivalate (Monomeric Analogue)

(+)-2-Methylbutyl pivalate was synthesized from pivalic acid and (–)-2-methylbutyl alcohol *via* pivaloyl chloride: bp 68°C (15 mm); $[\alpha]_D^{25} 19.2$ in *n*-heptane.

Polymerization

Radical Polymerization. Dry benzene (50 ml), monomer (8 g), and benzoyl peroxide (3.7×10^{-3} g) were sealed in a glass ampoule at 25°C under diminished pressure (1×10^{-4} mmHg) after degas-

sing. The ampoule was immersed in a water bath regulated at $40.0 \pm 0.1^\circ\text{C}$ for 48 hr. The reaction mixture was poured into an excess amount of methanol, and the polymer was dried by the freeze-drying technique from dioxane after reprecipitation and obtained as white powder (yield 70%); $[\eta] = 0.33$ dl/g (at 30°C, in cyclohexane).

Anionic Polymerization. Dry toluene (50 ml) and monomer (8 g) were added in a glass ampoule under nitrogen atmosphere and cooled down to -78°C . Then the ether solution of phenyl magnesium bromide (PhMgBr 1.5×10^{-3} mol Mg/ml, 2 ml) cooled to the same temperature, was added dropwise and after degassing, the ampoule was sealed under vacuum. The polymerization was carried out at -78°C for 8 hr. The polymer was obtained as transparent, rubbery solid from the reaction mixture by a method similar to that stated above (yield 20%); $[\eta] 0.37$ dl/g (at 30°C, in cyclohexane).

Photosensitized Polymerization. Dry toluene (10 ml), benzoin (6×10^{-2} g), and monomer (4 g) were sealed in an ampoule at 25°C under vacuum after degassing. This was exposed to a high intensity ultraviolet lamp at -40°C for 40 hr. The polymer was obtained as white powder from the reaction mixture by a method similar to that described above (yield 2.0%).

Poly(Methyl Methacrylate) and Monomeric Analogue. The isotactic and atactic poly(methyl methacrylate)s were obtained using PhMgBr and benzoyl peroxide, respectively, and were characterized by NMR. The former contained 100% of isotactic triad sequence and the latter consisted of 59.6% of syndiotactic and 32.7% of heterotactic sequences. Methyl pivalate was synthesized in the same as (+)-2-methylbutyl pivalate, bp 20°C (30 mm).

Measurements

ORD and UV spectra were measured on a JASCO ORD/UV-5 Spectropolarimeter. The measurements were performed between 400 and 205 m μ . Quartz cells of 10-mm path length were used. The cell was capped by a silicone rubber cap to prevent evaporation of the solvent, and through it a thermo-couple was immersed into the solution. Temperature of solutions was changed with a precision of $\pm 0.01^\circ\text{C}$ from room

temperature to a temperature 5°C below the boiling point of the solvent, by means of a water jacket.

n-Heptane, benzene, cyclohexane, dioxane, chloroform, and tetrahydrofuran were obtained as "Guaranteed" reagents and used as received. The lowest measurable limits of wave length were 210, 270, 210, 230, 220, and 210 m μ , respectively. "Spectro Grade" acetonitrile was also used and the lowest measurable wave length was 205 m μ .

Concentration of solutions for ORD measurements was 0.07 to 0.006 g polymer/ml and UV measurements were performed on solutions which contained 0.002 to 0.0005 g polymer/ml. After measurements at high temperatures, the solvent was evaporated and the concentration was determined by the gravimetric method. Increase in the concentration of the heated solution, compared with the original one, was below 0.5%.

Measurements of optical rotation (α) and extinction coefficient (k) on the single solution at the same temperature were carried out with a precision of 1/1000 and 5/1000, respectively. Values of optical rotation and absorbance of samples in solutions were obtained as the difference between those of solution and of blank (quartz and solvent).

IR and NMR spectra were measured on a JASCO MODEL DS-301 and a JMN-4H-100 (JEOL, 100 MHz) Spectrometer, respectively. Chloroform used for NMR measurements was purified by the usual means. NMR measurements were carried out on 12% solutions at 80°C using TMS as an internal reference.

RESULTS AND INTERPRETATION

IR and NMR Spectra

The chemical structures of PMBMA and the monomeric analogue are shown as follows

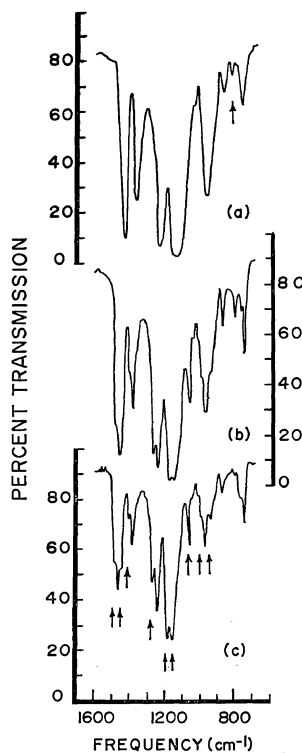
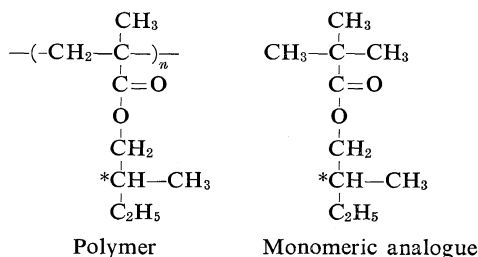


Figure 1. IR spectra of (a) isotactic, (b) atactic, and (c) syndiotactic PMBMA. Arrows indicate absorption peaks characteristic of polymers with different tacticities.

IR spectra of thin films of the unfractionated PMBMA obtained by anionic, radical, and photosensitized polymerizations are shown in Figure 1a—c. These spectra are similar to those of PMMA¹¹ which were polymerized by the same methods and whose tacticities were closely investigated. Comparing the IR spectra of these two poly(alkyl methacrylate)s, it is concluded that PMBMA obtained by anionic, radical, and photosensitized polymerization processes are isotactic (*i*-), atactic (*a*-) and syndiotactic (*s*-) polymers, respectively.

The absorption peak at 820 cm⁻¹ is characteristic of *i*-PMBMA. In the spectrum of *s*-PMBMA, peaks at 1060, 1270 cm⁻¹ and others are found as indicated by the arrows. The absorption bands at 1060 and 1385 cm⁻¹ correspond to those at 1063 and 1377 cm⁻¹¹¹ (or at 1058 and 1379 cm⁻¹¹²) of *s*-PMMA. Adopting the ratio of optical density D_{1060}/D_{1385} as a measure of

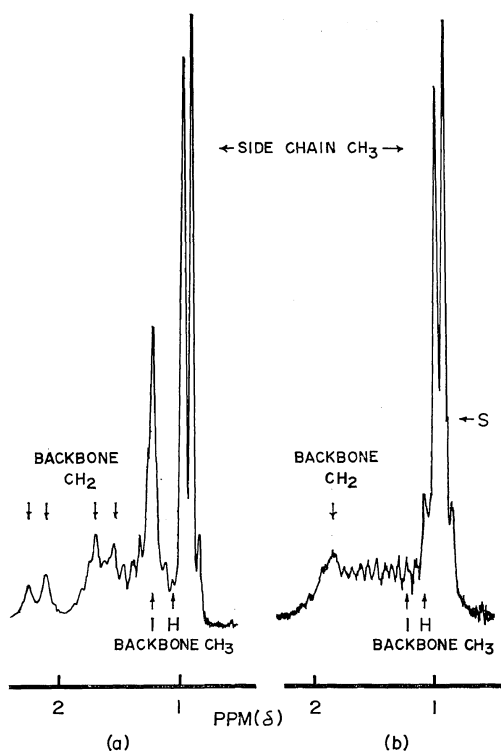


Figure 2. NMR spectra of (a) isotactic and (b) atactic PMBMA.

syndiotacticity,^{11,12} the ratio is calculated to be 0.95 for *s*-PMBMA. The IR spectrum of *a*-PMBMA is similar to that of the syndiotactic one. The ratio D_{1050}/D_{1385} is equal to 0.64 for *a*-PMBMA. It can be seen that *a*-PMBMA is abundant in syndiotactic triad sequences.

NMR spectra of *i*- and *a*-PMBMA are shown in Figure 2a and b, respectively (the spectrum of *s*-PMBMA could not be measured, because the yield of the polymer is so low that sufficient concentrated solution to measure the NMR spectrum could not be obtained). As seen from Figure 2, δ -values for the α -methyl protons attached to the molecular backbone in the iso- and heterotactic placements are 1.24 and 1.08, respectively. In the spectrum of *a*-PMBMA, an obscure shoulder at about 0.90 ppm is found which is considered to be the resonance peak of α -methyl protons in the syndiotactic placement.¹³ Unfortunately, we cannot determine the tacticity percentage correctly from the spectra obtained because of the overlap of the side-chain

methyl resonance and the α -methyl (especially that in syndiotactic placement) resonance. However, it can be estimated, by calculating roughly the intensity ratio of the resonance peaks, that *a*-PMBMA contains a comparatively high concentration of syndiotactic triad sequences. This is consistent with IR results.

Optical Rotatory Dispersion

The optical rotations of *i*- and *a*-PMBMA in various solvents depend linearly on the concentration of the polymer solution in the concentration range stated in the previous section.

The ORD curves of *i*- and *a*-polymers and of the monomeric analogue measured in *n*-heptane at 25°C in the wave length region of 400 to 250 $m\mu$ are shown in Figure 3. Similar curves were

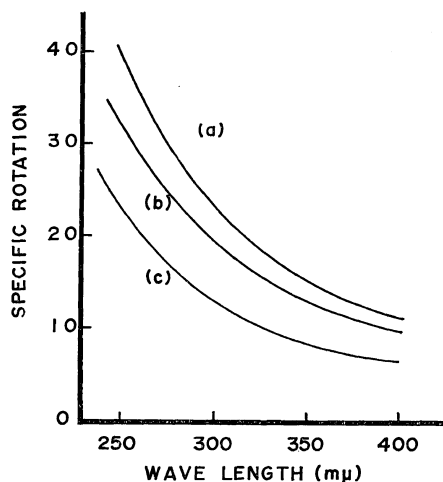


Figure 3. ORD curves of (a) isotactic PMBMA, (c) atactic PMBMA, and of (b) monomeric analogue measured in *n*-heptane at 25°C between 400 and 250 $m\mu$.

found for the other solvent systems and at each temperature. Klabunovskii, *et al.*⁴ investigated the ORD curves of PMBMA and found that there is a Cotton peak at about 290 $m\mu$ in each curve. However, all the ORD curves obtained in the present paper were plain.

Six kinds of solvents with different structures and polarities were used. The optical activity differs when the solvent is different (Table I), but systematic variations could not be found.

The optical activity of *i*-PMBMA is larger

ORD and UV of Poly[(+)-2-methylbutyl methacrylate]

Table I. Specific rotations at 300 m μ and 25°C of poly[(+)-2-methylbutyl methacrylate]s and (+)-2-methylbutyl pivalate in various solvents

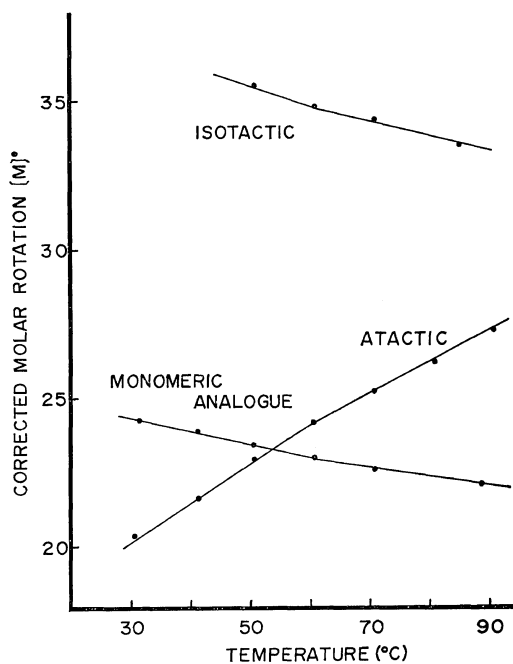
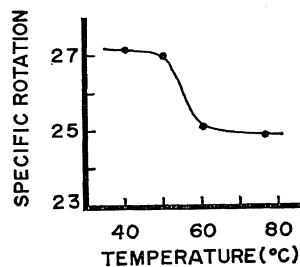
Polymerization process	<i>n</i> -Heptane	Benzene	Cyclohexane	Dioxane	Chloroform	THF
Anionic	23.6	20.1	19.0	19.9	23.3	20.6
Radical	12.7	15.1	12.8	11.4	16.2	12.1
UV	—	—	—	—	18.2	—
Mono. Anal.	19.2	20.0	—	16.8	20.3	16.0

and that of *a*-PMBMA is smaller than that of the monomeric analogue at the room temperature and at the same concentration in all solvents. The optical rotation of *s*-PMBMA measured in chloroform is slightly larger than that of *a*-PMBMA in the same solvent (Table I and Figure 3).

Temperature dependences of the corrected molar rotations* of the polymers and the monomeric analogue measured in *n*-heptane at 280 m μ and at every 10 degrees between 30 and 90°C are shown in Figure 4.

The corrected molar rotations of *i*-PMBMA and the monomeric analogue decrease with increasing temperature, while that of *a*-PMBMA increases with temperature. Similar relationships can be observed in the temperature dependence of uncorrected specific rotations measured at 280 m μ in dioxane (in this case, the correction was not carried out, because the refractive index in the UV region could not be obtained). The optical rotations of PMBMA and the monomeric analogue in the other solvent systems decrease

(or increase) discontinuously between 50 and 70°C, as shown in Figure 5, in which the


Figure 4. Temperature dependences of corrected molar rotations of PMBMA and monomeric analogue measured at 280 m μ in *n*-heptane.

Figure 5. Temperature dependence of specific rotation of isotactic PMBMA measured at 270 m μ in cyclohexane.

* It is necessary to correct the variation in the solvent refractive index caused by the temperature change, when the temperature dependence of the optical rotation is discussed. The correction was performed according to the method of Kauzmann, *et al.*,¹⁴ using the formula $[M]_{\lambda}^0 = [3/(n_{\lambda} + 2)][M]_{\lambda}$, where n_{λ} and $[M]_{\lambda}$ are the refractive index of solvent and the molar rotation measured at the wave length λ , and $[M]_{\lambda}^0$ is the molar rotation which the substance would have in a vacuum if its molecules were maintained in the same conformations that they have in solvent. Using the Lorentz-Lorenz equation and measuring the temperature dependence of solvent density, we can easily obtain $[M]_{\lambda}^0$ at each temperature. In the present case, Lauer's equation¹⁵ for *n*-heptane, $(n^2 - 1)^{-1} = 1.1235 - 0.01217\lambda^{-1}$ (at 25°C), was used to obtain the refractive index in the UV region.

Table II. Temperature coefficients of corrected molar rotation (for *n*-heptane) and of uncorrected specific rotations (for other solvents)

Solvents (measured at)	Low temperature range			High temperature range		
	Iso	Atact	Mono. Anal.	Iso	Atact	Mono. Anal.
<i>n</i> -Heptane (280 m μ)	-2.0×10^{-3}	5.7×10^{-3}	-1.7×10^{-3}	-1.4×10^{-3}	4.2×10^{-3}	-1.5×10^{-3}
Dioxane (270 m μ)	≈ 0	7.6×10^{-3}	-2.2×10^{-3}	≈ 0	5.1×10^{-3}	-1.9×10^{-3}

Solvents (measured at)	Iso	Atact	Mono. Anal.
Cyclohexane (270 m μ)	-2.9×10^{-3}	6.1×10^{-3}	-1.0×10^{-3}
Benzene (300 m μ)	≈ 0	≈ 0	-1.8×10^{-3}
THF (270 m μ)	≈ 0	≈ 0	-1.6×10^{-3}

temperature dependence of the specific rotation of *i*-PMBMA in cyclohexane is shown. These temperature variations are reversible and reproducible, and observable at every wave length between 350 and 250 m μ . Temperature coefficients $\Delta[M]^0/[M]^0\Delta T$ and $\Delta[\alpha]/[\alpha]\Delta T$ are summarised in Table II. Temperature coefficients of the polymers and the monomeric analogue are of the same order of magnitude (10^{-3}). It is interesting to note that absolute value of the temperature coefficient of each sample measured in the high temperature range (60 to 70°C) is smaller than that in the low temperature range (50 to 60°C) in the case of *n*-heptane and dioxane solutions.

Ultraviolet Spectra

UV spectra of *a*-PMBMA (in *n*-heptane, 300–210 m μ) and *a*-PMMA (in acetonitrile, 250–205 m μ) measured at about 30°C are shown in Figure 6a and b, respectively. Similar absorption curves without the fine structures were obtained for *i*-polymers and the monomeric analogues at every temperature.

The absorption peaks at about 210 m μ for the PMMA series and those at about 217 m μ for the PMBMA series arise from $n \rightarrow \pi^*$ electronic transitions of the carbonyl groups which are directly connected to the polymer main chain. The spectral shift in the UV absorption of both series of polymers (irrespective of varieties of tacticity) and of the monomeric analogues was not observed.

In the PMBMA series, the extinction coefficient (k) for *i*-polymer calculated from the maximum absorbance is larger than that for *a*-polymer,

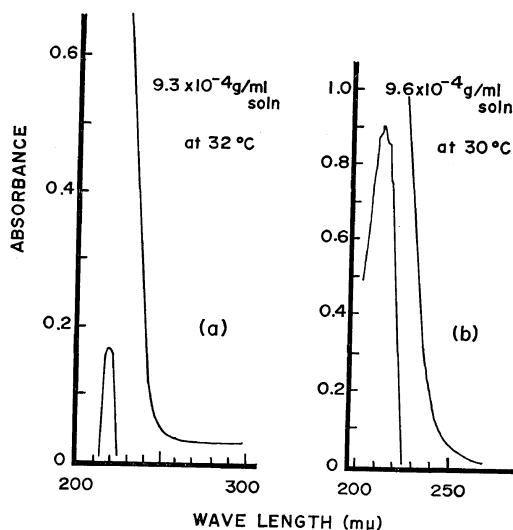


Figure 6. UV spectra of (a) atactic PMBMA in *n*-heptane and (b) atactic PMMA in acetonitrile.

while in the PMMA series, k for *i*-polymer is smaller than that of the atactic one at each temperature. The values of k for the monomeric analogues are smaller than those for the polymers (Figure 7). The values of k for the PMBMA series are smaller than those for the PMMA series.

Figure 7 shows the temperature dependences of k for the PMBMA and the PMMA series. The values of k decrease with increasing temperature. Temperature coefficients ($\Delta k/k\Delta T$) are also shown on each curve. The absolute values of $\Delta k/k\Delta T$ of *i*-polymers are greater, but on the other hand, those of *a*-polymers and (+)-2-methylbutyl pivalate are smaller in the high temperature range (60 to 70°C) than in the low

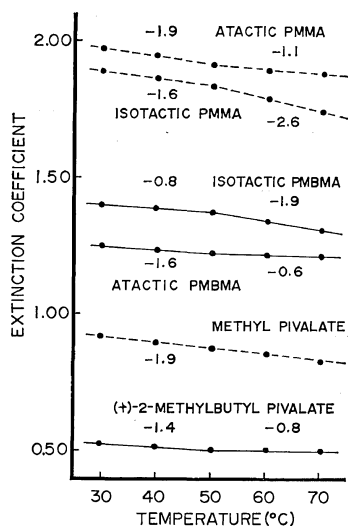


Figure 7. Temperature dependences of extinction coefficients of PMBMA and PMMA, and of monomeric analogues. Values described on each curve are values of $(\Delta k/k\Delta T) \times 10^3$.

temperature range (30 to 40°C).

Interpretation of Results

Generally speaking, when the special arrangements of successive monomeric units make the perturbation of the electronic states of the molecules greater and produce additional asymmetry of electronic states, UV spectra and the optical activity of the molecules may be significantly affected. If there is no spectral shift in the UV absorption (in the present case, and that absorption arose from the $n \rightarrow \pi^*$ transition, which is responsible for the optical activity) of chromophores in the different environments, a series of differences in optical properties is believed to originate from the conformational variations of the very local parts of the polymer chain.

In the PMBMA series, the optical activity and extinction coefficient of polymers and the monomeric analogue show significant differences from each other depending on the stereoregularity of the polymer. These differences may arise from the variety of the perturbations of chromophoric groups which are caused by chain winding and the local steric effects, as has been considered in the case of other optically active polymethacrylates.^{1,8} Differences in the optical

rotations of *i*- and *a*-PMBMA, and differences in those of the polymers and the monomeric analogue are, however, comparatively small. This is because the asymmetric carbon atoms are situated at δ -position with respect to the main chain, and, therefore, have no great influence on the conformational asymmetry of the polymer chain.

Such examples that the signs of the temperature coefficients of optical rotations of *i*- and *a*-polymers are different are very rare. The observed temperature dependences would arise from the fact that the equilibrium conformation which has a positive influence on the optical activity shifts to the less optically active conformation with increasing temperature in *i*-PMBMA. On the other hand, the reverse process occurs in *a*-PMBMA.

It is interesting to note that the temperature dependence of the optical rotation of the monomeric analogue is similar to that of *i*-polymer rather than that of *a*-polymer. The reason for this phenomenon is not clear at present.

In the UV spectra of both series of polymethacrylates, spectral shifts were not observed, even though the temperature of the solutions was changed. As seen from Figure 7, the numerical values of temperature coefficients of k cover the range $(-3 \text{ to } -0.6) \times 10^{-3}$ irrespective of differ-

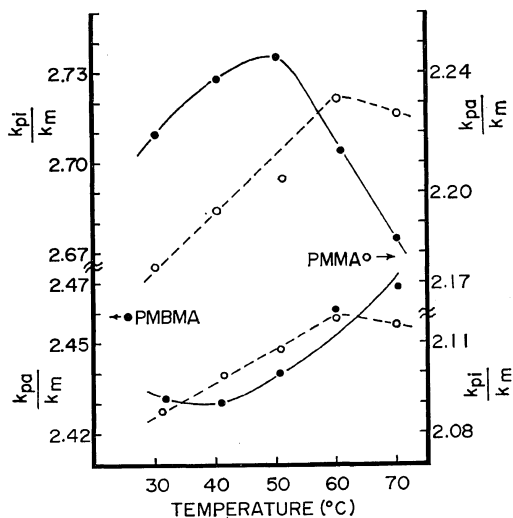


Figure 8. Temperature dependences of ratios of extinction coefficient of polymer to that of monomeric analogue.

ences in structures of the ester groups, in tacticity of polymers and also in spite of structural differences between the polymer and the monomeric analogue. If temperature variations of k for polymers arise only from the conformational changes of the comparatively long parts of the polymer main chain, these may not be observed in monomeric analogues. Further, if these variations are based on the conformational changes of the ester alkyl groups, these may not be found in the case of methyl esters. The variations are observed in the same way for all samples. Therefore, it may be considered that the common phenomena arise from the local conformational changes, perhaps including the variations in the conformational characteristics of -COO groups.

Defining briefly hyperchromity as the ratio of the extinction coefficient of a polymer (k_p) to that of the corresponding monomeric analogue (k_m), the values of k_p/k_m were calculated, and in Figure 8 these values are plotted *vs.* temperature.

The ratio increases with temperature and begins to decrease at about 50°C in *i*-PMBMA, while that in *a*-PMBMA decreases until 40°C and then increases. It is interesting to compare these data with the temperature dependence of the specific rotation in which we can observe the decrease of the absolute values of temperature coefficients at about 60°C and the opposite temperature variation between *i*- and *a*-polymers. The ratios of *i*- and *a*-PMMA increase with increasing temperature until 60°C and then begin to decrease.

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