Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Preparation and Properties of Poly(Quinazolone-Imide)S

Akira Fukami[a]; Katsuyoshi Iisaka[b]; Sigeru Kubota[b]
[a] Optec D.C. Melco Laboratory Co., Ltd., Higashikurume, Japan [b] Materials and Electronic Device Laboratory Mitsubishi Electric Corporation, Amagasaki, Japan

To cite this Article Fukami, Akira , Iisaka, Katsuyoshi and Kubota, Sigeru(1990) 'Preparation and Properties of Poly(Quinazolone-Imide)S', Journal of Macromolecular Science, Part A, 27: 2, 179 — 192
To link to this Article: DOI: 10.1080/00222339009351495
URL: http://dx.doi.org/10.1080/00222339009351495

J. MACROMOL. SCI.—CHEM., A27(2), pp. 179-192 (1990)

PREPARATION AND PROPERTIES OF POLY(QUINAZOLONE-IMIDE)S

AKIRA FUKAMI*

Optec D.C. Melco Laboratory Co., Ltd.
203 Higashikurume, Japan

KATSUYOSHI IISAKA and SIGERU KUBOTA

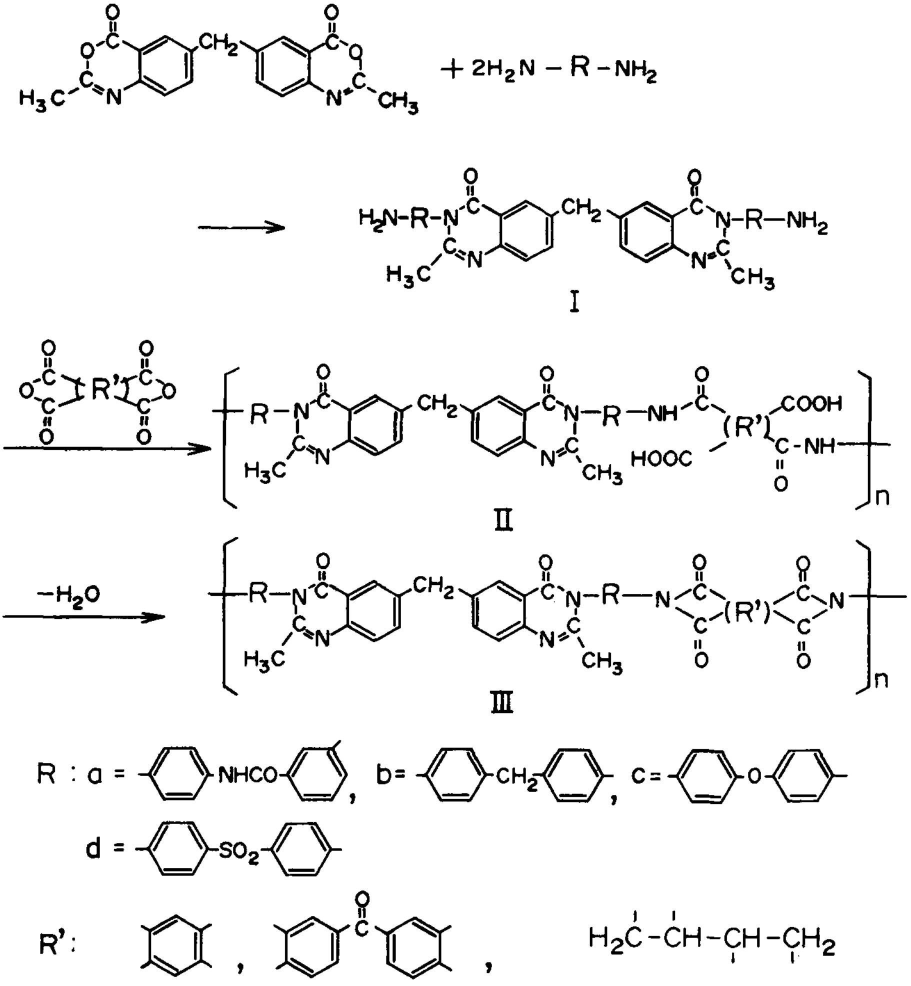
Materials and Electronic Device Laboratory
Mitsubishi Electric Corporation
661 Amagasaki, Japan

ABSTRACT

Poly(quinazolone-imide)s (III) were prepared from poly(quinazolone-amic acid)s (II), which were obtained from pyromellitic dianhydride (PMDA), benzophenonetetracarboxylic acid dianhydride (BTDA), or 1,2,3,4-butanetetracarboxylic dianhydride (BTCA), and diaminoquinazolones (I). The latter were synthesized from 6,6'-methylenebis(2-methylbenzoxazin-4-one) and various other aromatic diamines. Many of the resulting films of III were flexible and tough. The electrical, mechanical, and thermal properties of these polymer films were determined. The glass-transition temperatures of III obtained from PMDA and BTDA were 265–323°C, i.e., higher than the T_g of polyquinazolone, and lower than that of polyimide. It has been found that the bisquinazolone structure is more effective than imide in decreasing T_g. Comparison of III obtained from PMDA and BTDA showed the former to have higher T_g. It is evident from the mechanical strength results, thermogravimetric analysis, and IR spectra that bisquinazolone structure is less resistant toward thermal oxidation than the imide unit.

INTRODUCTION

Many polymers, such as polyimide, polybenzimidazole, polybenzoxazole, and polyquinazolone, have been studied because macromolecules with hetrocyclic rings in the main chain exhibit good thermal stability. However, for practical use, structures with efficient processing properties, such as thermostability, plasticity, and solubility, are often desired. To this end, polyamideimide, polyesterimide, and polysiloxaneimide have been synthesized and have been proved to be effective.



I

II

III

The present authors investigated the properties of polyquinazolones and proved their good solubility and excellent thermal stability [1]. In this paper the preparation and the properties of polyimides with quinazolone rings are reported.

EXPERIMENTAL

Monomers

Pyromellitic dianhydride (PMDA) was used after sublimation, mp 285°C. 3,3′,4,4′-Benzophenone tetracarboxylic acid dianhydride (BTDA) and 1,2,3,4-butanetetracarboxylic acid dianhydride (BTCA) were recrystallized: mp BTDA 236°, BTCA, 265°C.

The aromatic diamines used in this experiment are 3,4′-diaminobenzanilide (DABA), 4,4′-diaminodiphenylmethane (DADPM), 4,4′-diaminodiphenyl ether (DADPE), and 4,4′-diaminodiphenyl sulfone (DADPS). DABA was synthesized by the method previously reported [2] (mp 155°C; from Ref. 2, 155°C). DADPM, DADPE, and DADPS were obtained from commercial sources and purified by recrystallization from ethanol.

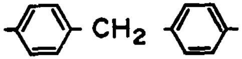
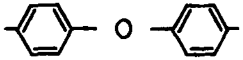
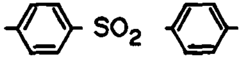
Synthesis of Diaminoquinazolone, I

Bisbenzoxazinone (6,6′-methylenebis(2-methylbenzoxazin-4-one)) (0.010 mol) was dissolved in 50 mL *m*-cresol, and a *m*-cresol (50 mL) solution containing 0.050 mol of the aromatic diamine was subsequently added. I was obtained by slowly heating the reaction mixture at 100 and 150°C for 2 h each and at 180 and 200°C for 1 h each. The resulting solutions of the products, I_a, I_c, and I_d, were poured into ethyl ether, while the solution of I_b was poured into methanol at room temperature, and the precipitates were filtered off. The precipitate of I_a was washed with acetone, and those of I_b, I_c, and I_d were washed with methanol to strip off the excess unreacted diamine. They were heated for 2 h at 50°C in 5% aqueous sodium hydroxide, and unreacted bisoxazinone was removed. Their characteristics are listed in Table 1.

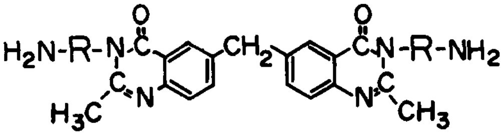
Polymerization

All of the poly(quinazolone-imide)s were synthesized by solution polymerization at a concentration of 10 to 20% solid in dimethylacetamide (DMA).

TABLE 1. Synthesis of Diaminoquinazolones

Diamino-quinazolone	R[a]	Yield,[b] %	mp,[c] °C	Elemental analysis, % Calculated[d] C	H	N	Found C	H	N
I_a		81.2	185	71.80	4.82	14.88	71.50	4.71	14.62
I_b		90.3	188	77.81	5.48	12.10	77.70	5.26	12.42
I_c		86.8	173	73.91	4.91	12.03	73.51	4.81	11.74
I_d		82.0	208	64.97	4.31	10.57	64.81	4.13	10.88

[a]



[b] Calculated from diaminoquinazolone equivalent to bisbenzoxazinone.

[c] Melting point by capillary method.

[d] Calculated for formula I.

Diaminoquinazolone I (0.01 mol) was dissolved into DMA until its final polymer concentration became 20 wt% at 30°C, and 0.01 mol of powdered acid dianhydride was added to the solution in several portions. The resulting solution immediately became viscous. The intrinsic viscosity of Polymer II was determined at 25°C in DMA. Polymers III were obtained as films on imidization by heating II.

Infrared Spectra of the Polymers

The solution of Polymer II was cast onto an IR cell plate and heated for 1 h at 100 and 150°C, and for 4 h at 200°C. An example of the resulting IR spectra is shown in Fig. 1.

The spectra of Polymers III_c-3 and III_c-7 exhibited absorption bands due to the imide group at 1780, 1720, 1370, and 720 cm^{-1}, while absorption of the amide group in the neighborhood of 3300, 1650, and 1540 cm^{-1} disappeared completely [3, 4].

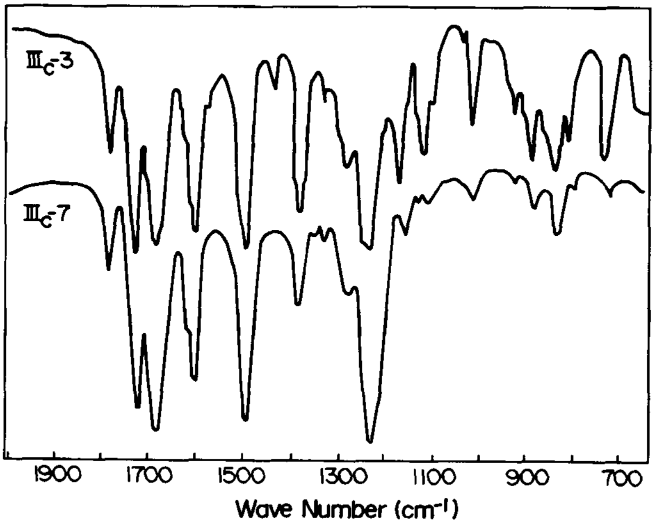


FIG. 1. IR spectra of poly(quinazolone-imide)s III_c-3 and III_c-7.

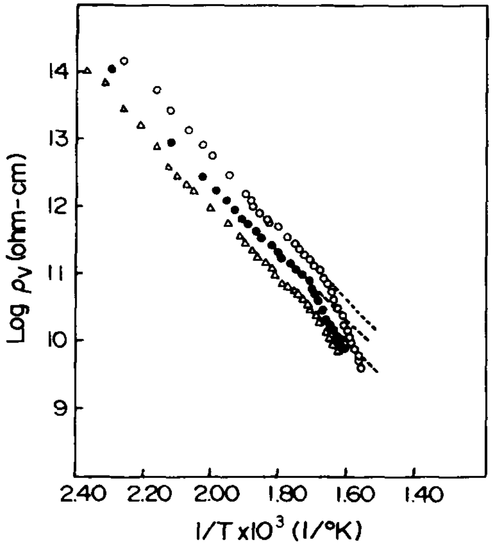


FIG. 2. Temperature dependence of volume resistivity for poly(quinazolone-imide)s: (Δ) III_a-1; (○) III_b-2; (●) III_b-3.

Characterization of Films

DMA solution of poly(quinanzolone-amic acid) II was coated onto a thin plate and heated by a method similar to that indicated above and converted to III. The films were removed by the mercury amalgam process and washed with concentrated hydrochloric acid. After being washed several times with water, they were dried at 250°C for 3 h.

Measurements of tensile strength and elongation were obtained with an automatic tensile testing machine (Shimadzu Corporation Automatic graph IM-100). The stretching rate was 10 mm/min, and the sample size was 80 × 5 mm.

Dielectric constants (ε), dielectric loss (tan δ), and volume resistivities (ρ_v) were measured at 200 V and 60 Hz from room temperature to 200°C.

Dynamic thermogravimetric analyses (TGA) were performed in air and in a 20-mL/min stream of nitrogen with a Shimazu thermal analyzer. The heating rate was 5°C/min and the sample size was 10 mg of film. Isothermal weight loss experiments were performed in air at 250°C.

RESULTS AND DISCUSSION

Preparation of Poly(Quinazolone-Imide)s

Diamines I containing quinazolone rings were synthesized by the reaction of bisoxazinon and diamine. Poly(quinazolone-amic acid)s II were obtained by the reaction of diamine I and PMDA, BTDA, or BTCA in DMA at room temperature. In the case of PMDA, II gave high viscosities when the mole ratio of PMDA to diamine I_a, I_b, and I_c was near 1.0. PMDA was used with stepwise additions of 80 and then 20 molar quantities, as the viscosity increase was affected by the polymerization procedure. As for PMDA and I_d from DADPS, various concentrations were used, but high viscosity was never obtained. The polymers synthesized are listed in Table 2.

In a comparison study of the reactivity of the acid anhydrides, the reaction of BTDA and I can be conducted at 15-20% concentration, and the resulting product is superior to that of PMDA in solubility. High viscosity was not obtained in the reaction of I_d and BTDA. It is clear that the introduction of the sulfonyl group causes a decrease in the amino group reactivity [5].

In case of BTCA, the reaction was carried out at concentrations above 20% solid in DMA, but high viscosities were not obtained.

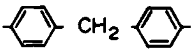
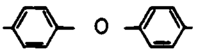
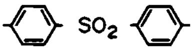
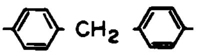
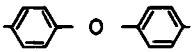
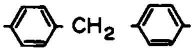
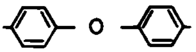
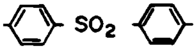
It is known that the viscosity of polyamide acid solution decreases gradually when it is kept at room temperature [6]. However, the intrinsic viscosities of II solutions at 20°C decreased only by 10% after 30 days, i.e., they were relatively stable compared with poly(pyromellitic-amic acid) solutions.

Kurosaki [7] explained that, in the preparation of poly(imidazole-imide), the basicity of the imidazole ring is effective in stabilizing the viscosity of the solution due to its interaction with the carboxyl group of pyromellitic-amic acid. In a previous paper [1] on the preparation of polyquinazolones, their solubilities were studied and it was found that the introduction of quinazolone rings results in increased solubility in phenolic solvents. Hence the same features seem to determine the viscosity stability of poly(quinazolone-amic acid).

Properties of Poly(Quinazolone-Imide)s

Polymers from PMDA, BTDA, and I_d, and polymers from BTCA and I_b, I_c, and I_d could not be cast into films. However, the other films showed

TABLE 2. Preparation of Poly(Quinazolone-Amic Acid)s

Polymer II[a]				Film	N, %	
	Dianhydride	R	η_{inh}[b]	properties[c]	Calc[d]	Found
II_a-1	PMDA		1.23	+	11.99	11.84
II_b-2	PMDA		1.02	+	9.58	9.35
II_c-3	PMDA		1.31	+	9.54	9.63
II_d-4	PMDA		0.31	–	8.60	8.62
II_a-5	BTDA		1.24	+	10.78	11.00
II_b-6	BTDA		1.06	+	8.57	8.48
II_c-7	BTDA		1.41	+	8.53	8.60
II_d-8	BTDA		0.24	–	7.77	7.62
II_b-9	BTCA		0.20	–	10.05	10.20
II_c-10	BTCA		0.37	–	10.00	9.78
II_d-11	BTCA		0.10	–	8.97	8.75

[a] Formula II.

[b] Measured at a concentration of 0.5 g/100 mL in DMA at 25°C.

[c] +, flexible; –, brittle.

[d] Calculated from Formula III.

TABLE 3. Mechanical Properties of Poly(Quinazolone-Imide)s at 20°C

	Initial		After aging for 168 h at 220°C	
Polymer	Tensile strength, kg/ mm^2	Elongation, %	Tensile strength, kg/mm^2	Elongation, %
III$_a$-1	11.9	7.0	9.0	5.4
III$_b$-2	69	3.9	6.0	3.0
III$_c$-3	10.5	6.0	8.5	5.5
III$_a$-5	10.2	6.7	8.7	3.8
III$_b$-6	9.0	4.5	7.8	3.5
III$_c$-7	10.0	7.0	8.8	4.0

flexibility and toughness (Table 3). When poly(quinazolone-imide) III$_a$, III$_b$, and III$_c$ were heated in air at 250°C for 168 h, they became colored and less flexible. After aging at 220°C, the polymers remained almost unchanged in appearance, but the film strength declined to 75–89% of the initial value. There was little difference in the thermal degradation of polymers with varying R units. These results indicate that the methylenebisquinazolone moiety is less thermally stable than the imide group.

Dielectric properties are listed in Table 4 and the electrical resistivity is shown in Fig. 2. Few changes are observed for ε and $\tan \delta$ up to 200°C. The resisitivity shows linear $\log \rho_v$ vs $1/T$ plots above 120°C, but in the range of 265–323°C ($1/T = 1.86 \times 10^{-3}$ to 1.68×10^{-3}), clear changes of slope ob-

TABLE 4. Dielectric Properties of Poly(Quinazolone-Imide) Films[a]

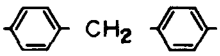
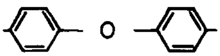
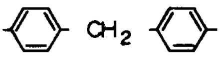
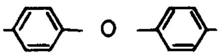
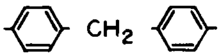
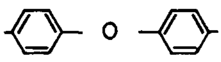
	25°C		100°C		150°C		200°C	
Polymer	ε	tan δ, %	ε	tan δ, %	ε	tan δ, %	ε	tan δ, %
III$_a$-1	3.10	0.65	2.54	0.70	2.54	0.80	2.50	0.87
III$_b$-2	3.20	0.28	3.50	0.23	3.40	0.21	3.41	0.30
III$_c$-3	3.60	0.20	3.00	0.24	3.00	0.23	3.11	0.26
III$_a$-5	3.15	0.54	3.16	0.61	3.16	0.60	3.19	0.62
III$_b$-6	3.10	0.30	3.14	0.30	3.20	0.31	3.18	0.33
III$_c$-7	3.43	0.28	3.44	0.28	3.43	0.30	3.45	0.31

[a] Measured at 200 V and 60 Hz.

served, which can correspond to glass transition temperatures T_g [8] (see Table 5).

From these results it is evident that the T_g of polymers increases when an imide group is introduced into polyquinazolones (by 65–68°C in the case of the imide from PMDA), and that the imide moiety has an effect on the stiffness of the main chain. In comparing polymers from PMDA and BTDA (III_a-1 vs III_a-5, III_b-2 vs III_b-6, III_c-3 vs III_c-7), the latter show T_g lower by around 35°C, while the substituents in both PMDA and BTDA

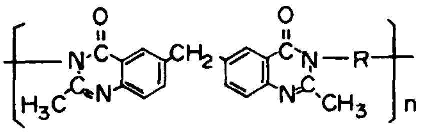
TABLE 5. Transition Temperature of Poly(Quinazolone-Imide)s III and Polyquinazolones

Polymer	Dianhydride	R[a]	T_g[b] °C
III_a-1	PMDA		300
III_b-2	PMDA		323
III_c-3	PMDA		311
III_a-5	BTDA		265
III_b-6	BTDA		286
III_c-7	BTDA		274
Polyquinazolone	Q-1[c]		214
Polyquinazolone	Q-2[c]		258
Polyquinazolone	Q-3[c]		238

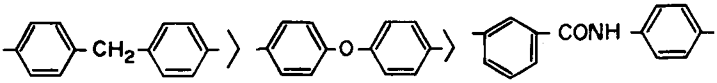
[a] Formula III.

[b] Measured from temperature dependence of electrical resistivity.

[c] Polyquinazolone,



polymers appear to affect T_g in the following decreasing order:



Tobolsky reported the effect of diamine and acid components on the T_g of polyimides in tan δ studies [9], and our results agree with his conclusion. However, there is little difference in the T_g compared with the results of Tobolsky. This is explained by the effect of the methylenebisquinazolone unit.

Thermal stability was measured by TGA (Fig. 3). In Polymers III_c-3 and III_c-7, thermal degradation began above 400°C. There is little difference in the thermal degradation behavior up to 500°C under nitrogen and air, but the weight loss at 600°C is much larger in air. Polymer III_c-10 started to decompose at around 350°C and reached a 50% weight loss at 500°C. In a comparison of the dianhydride components, polymers from BTDA began to decompose at lower temperature than those from PMDA and showed higher weight losses. However, the thermal stability of III_a, III_b, and III_c is affected least by the structure of the diamines in them.

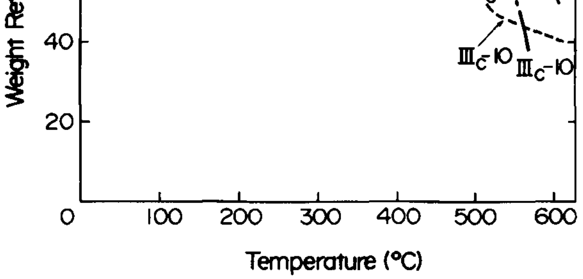


FIG. 3. TGA curves of poly(quinazolone-imide) films. Heating rate 5°C/min.

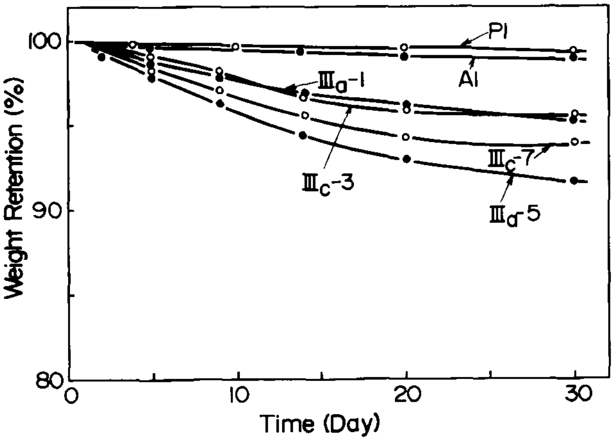
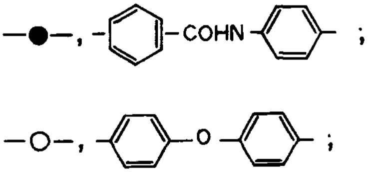
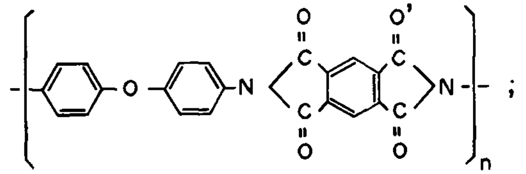


FIG. 4. Isothermal weight loss of poly(quinazolone-imide) and polyimide films in air at 250°C. Film thickness 30 μm.

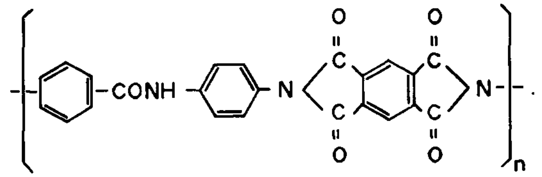
R:



PI,



AI,



The isothermal weight loss of poly(quinazolone-imide) III_a-1, III_a-5, III_c-3, and III_c-7 in air at 250°C is shown in Fig. 4. In order to decide the trend in the thermal stability, polyimide films PI and AI obtained from PMDA with the same diamines as DADPA and DABA were also studied. In the aging of polyimides PI and AI for 30 days at 250°C, the weight loss was 2% or less, and few changes were observed in the appearance of the films and the flexibility. However III_a and III_c lost 4–9% of their weight and their flexibility. Accordingly, the data in air indicate that the introduction of quinazolone rings in the polyimide decreases the thermal stability, as mentioned above. Polymers III_a-1, III_a-5, III_c-3, and III_c-7 were flexible after being heated at 220°C for 30 days, and few apparent changes were observed while their weight loss was below 4%. It is clear from the results of III_a and III_c that better thermal stability is obtained from any acid components with PMDA than with BTDA.

The infrared spectra of films of poly(quinazolone-imide) III_c-3 were measured after heating in air (Fig 5). As the temperature rose up to 350 and 380°C, the spectra exhibited a decrease in absorptions at 1680 and

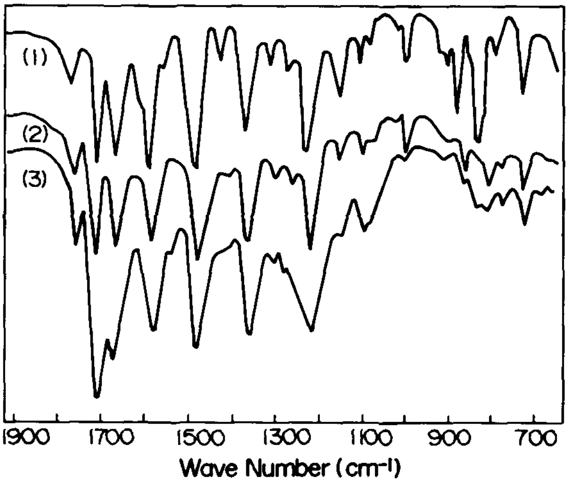


FIG. 5. IR spectra of poly(quinazolone-imide) films III_c-3. (1) Original III_c-3, (2) degraded at 350°C, (3) degraded at 380°C. Heating rate 2°C/min in air.

1590 cm^{-1} due to the quinazolone ring. However, the absorption bands at 1780, 1720, 1380, and 723 cm^{-1} of the imide ring did not change. The variation in the thermoxidative stability of poly(quinazolone-imide)s will, therefore, be primarily due to the degradation reaction in the methylenebisquinazolone structure.

REFERENCES

[1] A. Fukami, *Kogyo Kagaku Zashi, 73,* 1239 (1970).
[2] J. Preston and R. W. Smith, *Polym. Lett., 4,* 1033 (1966).
[3] S. Nishizaki and A. Fukami, *Kogyo Kagaku Zashi, 66,* 382 (1963).
[4] C. E. Sroog, A. V. Abramo, C. E. Berr, and K. L. Oliver, *J. Polym. Sci., A3,* 1373 (1965).
[5] K. Kuze, *Kogyo Kagaku Zashi, 72,* 1603 (1969).
[6] L. W. Frost and I. Keese, *J. Appl. Polym. Sci., 8,* 1039 (1964).
[7] J. Kurosaki, *Polym. Prepr. Jpn., 16,* 433 (1964).
[8] R. W Warfield, *SPE J., 17* (4), 364 (1961).
[9] A. V. Tobolsky, *Text. Res. J.,* p. 1110 (1965).

Received December 31, 1988