Thermal Degradation and Electrical Properties of Random and Block Piperazine Copolyamides

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Summary

The thermal degradation of random and block copolymers of terephthaloyl *trans*-2,5-dimethylpiperazine/isophthaloyl *trans*-2,5-dimethylpiperazine were investigated in terms of rates, activation energies, degradation products, and electrical properties. The rates of degradation and the nature of the volatile degradation products indicate that both random and block copolymers follow a nearly random free-radical type of cleavage in vacuum with activation energies between 59 and 61 kcal/mole. In the temperature range 390–440°C, the block copolymers are significantly more stable in a vacuum (the rates of degradation are two to four times slower) than the random copolymers. In contrast to the random copolymers, the block copolymers showed only slight frequency dependence of their dielectric constants and dissipation factors between 0.1 and 100 kcps.

Previous papers dealt with the thermal degradation of a series of piperazine polyamides (*1–3*). It was found that methyl substitution of the piperazine rings of the polymers decreases their thermal stability of the system in a vacuum, whereas the presence of terephthaloyl moieties (polycondensation in the para positions of the acid component) increases the thermal stability in comparison with the system having isophthaloyl moieties in the polymer chains (polycondensation in the meta positions of the acid component). The high activation energies, the nature of the volatile degradation products, and the character of the rate curves indicated essentially random thermal breakdowns.

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The present investigations deal with the thermal and electrical properties of random and block copolymers of terephthaloyl *trans*-2,5-dimethylpiperazine/isophthaloyl *trans*-2,5-dimethylpiperazine.

EXPERIMENTAL DETAILS

Materials

The random copolymers of terephthaloyl *trans*-2,5-dimethyl-piperazine/isophthaloyl *trans*-2,5-dimethylpiperazine were prepared in chloroform and with excess diamine as the acceptor by the low-temperature polycondensation method described by Morgan and Kwolek (4).

The block copolymers were made by a method similar to that described for the preparation of the ordered (block) copolyamide of terephthaloyl *trans*-2,5-dimethylpiperazine/sebacyl *trans*-2,5-dimethylpiperazine (4).

Viscosity Measurements

The inherent viscosities [$(\ln \eta_{rel})/C$, where $C = 0.5$ g/100 ml] were determined in *m*-cresol at $30 \pm 0.05°C$ with Cannon-Fenske viscometers and varied between 1.5 and 2.2. These values correspond to a number of average molecular weight range (3) of approximately 20,000–30,000.

Thermogravimetry

The thermogravimetric studies were carried out with samples of 3–7 mg in a vacuum ($\sim 10^{-5}$ mm Hg) using a Cahn RG electrobalance (1–3).

Mass Spectrometric Analyses

The collection and subsequent mass spectrometric analyses of the degradation products volatile at room temperature were carried out by a method already described (1,2).

Electrical Measurement

The dielectric properties of the polymers were measured on 1-in.-diameter disks by the air-displacement method (5) with a General Radio Corporation 1610-A capacitance measuring assembly and a 1690-A sample holder.

RESULTS AND DISCUSSION

The random and block copolymers are composed of units of terephthaloyl *trans*-2,5-dimethylpiperazine,
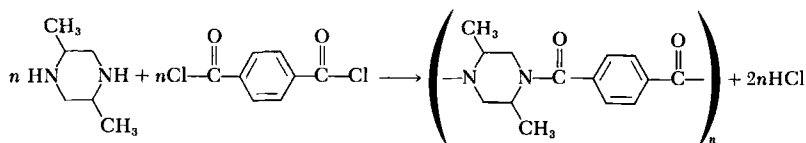
and isophthaloyl *trans*-2,5-dimethylpiperazine,
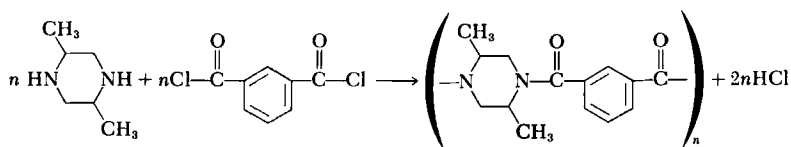
Poly(isophthaloyl *trans*-2,5-dimethylpiperazine) homopolymer melts around 320°C, while poly(terephthaloyl *trans*-2,5-dimethylpiperazine) shows no melting below 420°C. Experiments conducted with a Perkin-Elmer differential scanning calorimeter (Model DSC-1B) indicate that the apparent melting range of the latter homopolymer coincides with its degradation temperature (450–475°C). Neither homopolymer shows a second-order glass transition, which is apparently due to chain stiffness. X-ray diffraction patterns indicate essentially no crystallinity for poly(isophthaloyl *trans*-2,5-dimethylpiperazine), and no melting endotherm was observed for this polymer by differential scanning calorimetry. In view of the fact that the apparent melting range of one of the homopolymers and some of the copolymers coincide with their degradation points, only rough melting point vs. composition plot could be constructed in support of the copolymer structures and compositions. However, it appears that a "eutectic point" is reached at approximately 300–310°C with the random copolyamide containing 60 mole % terephthaloyl *trans*-2,5-dimethylpiperazine. In contrast to the block copolymers, the random copolymers are soluble in a mixture of chloroform–methyl alcohol, further reflecting the differences in the copolymer structures and compositions.

Thermal Degradation in Vacuum

The rates of degradation were studied by isothermal thermogravimetry with a Cahn RG electrobalance (*1–3*). Figures 1 to 4

FIG. 1. Thermal degradation of 50/50 mole % random copolymer of tere-phthaloyl *trans*-2,5-dimethylpiperazine/isophthaloyl *trans*-2,5-dimethyl-piperazine.
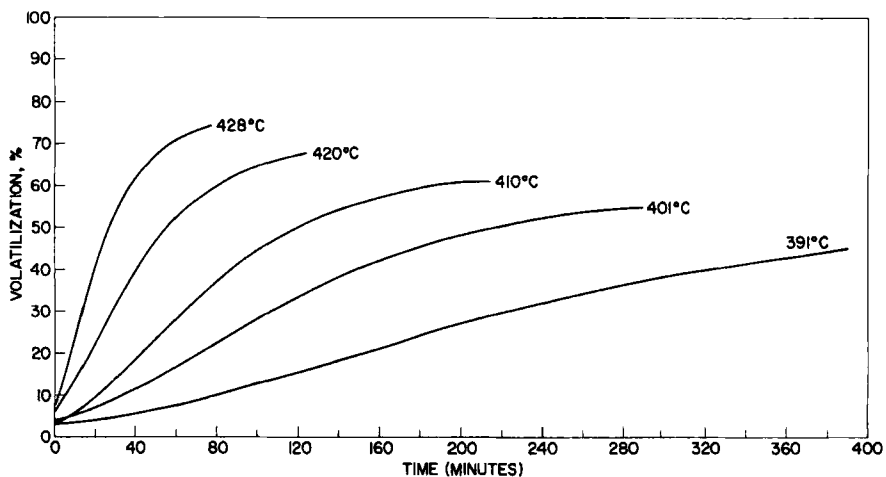
FIG. 2. Thermal degradation of 50/50 mole % block copolymer of tere-phthaloyl *trans*-2,5-dimethylpiperazine/isophthaloyl *trans*-2,5-dimethyl-piperazine.
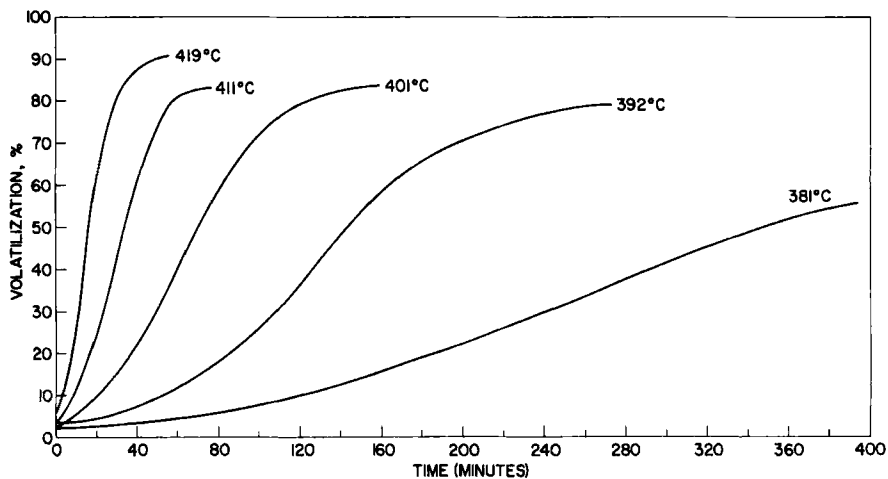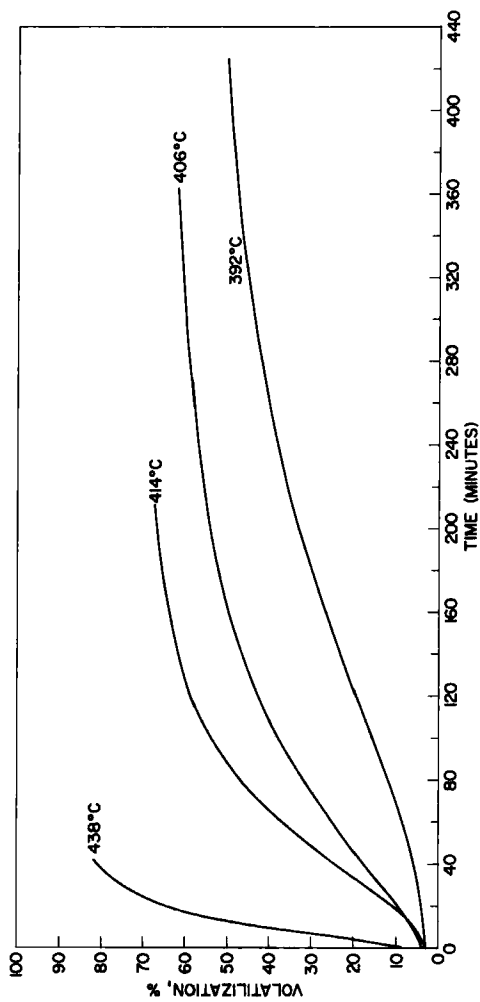
FIG. 3. Thermal degradation of 70/30 mole % random copolymer of terephthaloyl *trans*-2,5-dimethylpiperazine/isophthaloyl *trans*-2,5-dimethylpiperazine.
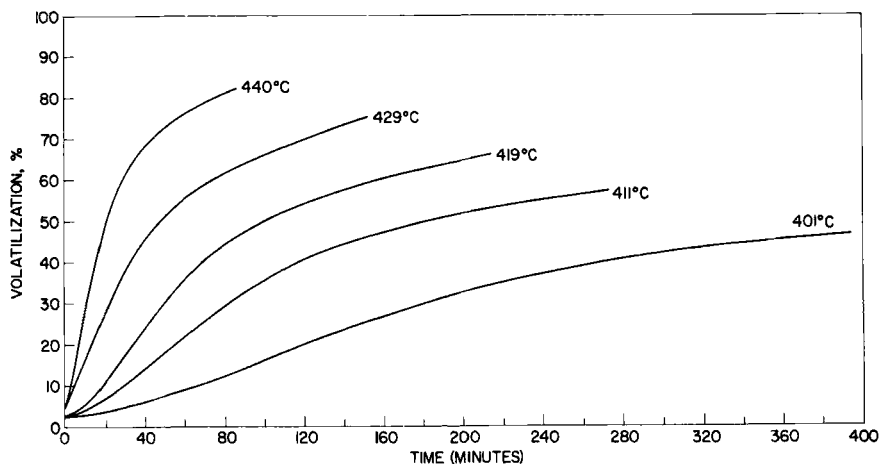
FIG. 4. Thermal degradation of 70/30 mole % block copolymer of tere-phthaloyl *trans*-2,5-dimethylpiperazine/isophthaloyl *trans*-2,5-dimethyl-piperazine.

show the percentage volatilization as a function of time at various temperatures for the random and block copolymers. Zero time denotes the start of the isothermal heating period, which was usually reached within 15 to 20 min after the preheated furnace was positioned around the sample tube. The small weight losses that occur prior to the attainment of isothermal conditions are most likely due to the loss of absorbed moisture in the polymers. The corresponding rates were calculated from the volatilization-times curves and are illustrated by Figs. 5 to 8. Since it was previously shown (3) that the rates of volatilization of the poly(isophthaloyl *trans*-2,5-dimethylpiperazine) homopolymer are independent of molecular weight in the range 12,000–40,000, it was assumed that a similar situation prevails in the case of the copolymers. The 50:50 mole % random copolymer shows maxima in the rate curves at approximately 40% volatilization (Fig. 5), whereas the other copolymers exhibit maxima between 20 and 30% volatilization (Figs. 6 to 8). In previous publications (1–3) it was shown that the homopolymers of poly(terephthaloyl *trans*-2,5-dimethylpiperazine) and poly(iso-phthaloyl *trans*-2,5-dimethylpiperazine) degrade according to a random-type cleavage with only slight influence of hydrolytic processes. Random-type degradations are characterized by the appearance of maxima in the rate curves at about 26% conversion

FIG. 5. Rates of thermal degradation of 50/50 mole % random copolymer of terephthaloyl   *trans*-2,5-dimethylpiperazine/isophthaloyl   *trans*-2,5-di-methylpiperazine.

(6). However, ample experimental evidence exists showing that the position of the maxima could shift to higher conversions if the polymer breakdown is influenced by nonrandom processes (7,8).

In general the maxima of the rate vs. conversion plots can be used as the rate constants for the calculation of the overall activation

FIG. 6. Rates of thermal degradation of 50/50 mole % block copolymer of terephthaloyl   *trans*-2,5-dimethylpiperazine/isophthaloyl   *trans*-2,5-di-methylpiperazine.

FIG. 7. Rates of thermal degradation of 70/30 mole % random copolymer of terephthaloyl *trans*-2,5-dimethylpiperazine/isophthaloyl *trans*-2,5-dimethylpiperazine.

energy of the polymer degradation (9). If the rate vs. conversion curves display linear portions beyond the maxima, it is preferable to extrapolate to 0% conversion to obtain the apparent initial rates. Such an extrapolation assures that the polymers which are being pyrolyzed have initially the same compositions (9). In the present
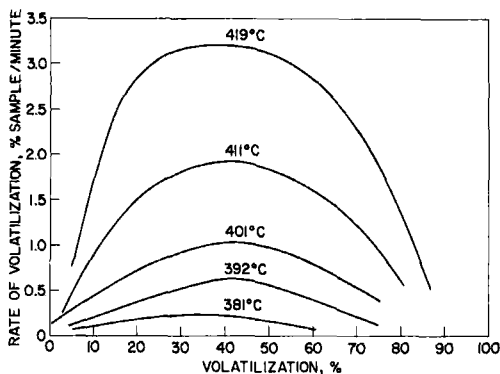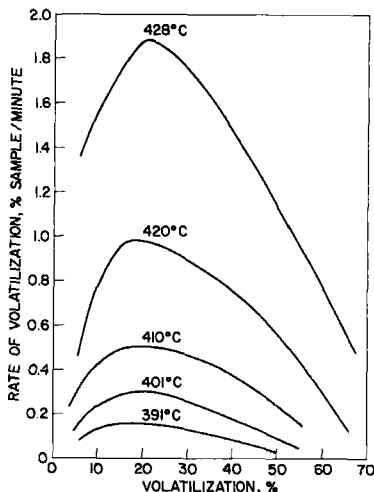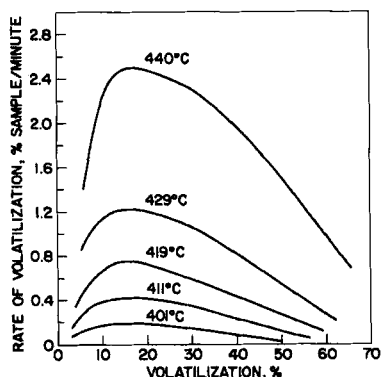

FIG. 8. Rates of thermal degradation of 70/30 mole % block copolymer of terephthaloyl *trans*-2,5-dimethylpiperazine/isophthaloyl *trans*-2,5-dimethylpiperazine.
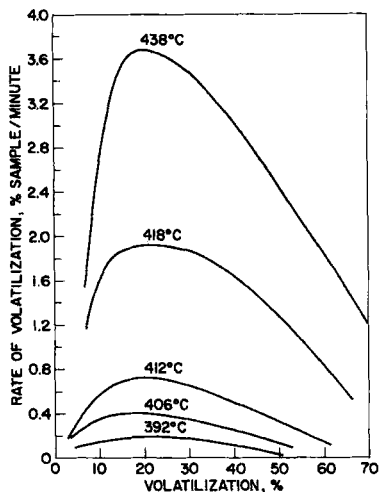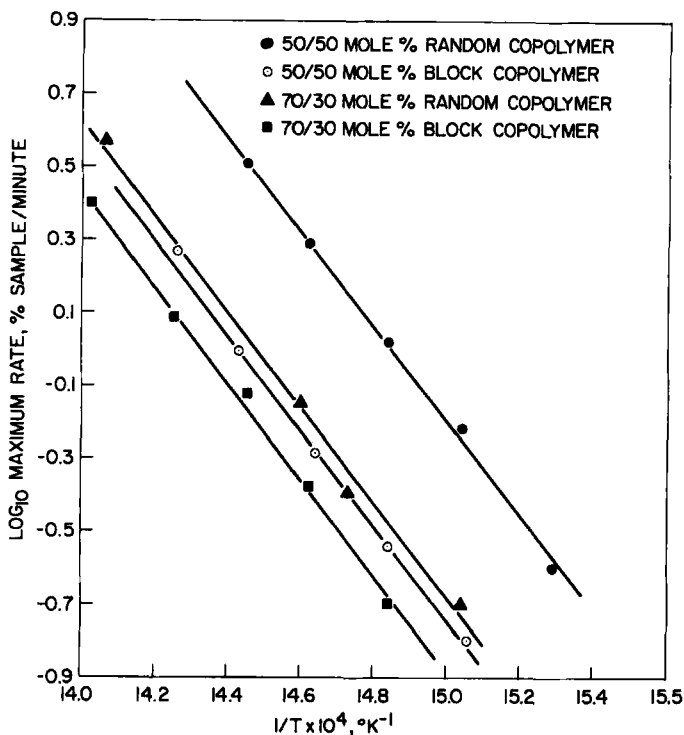
FIG. 9. Arrhenius plot for thermal degradation of random and block copolymers of terephthaloyl *trans*-2,5-dimethylpiperazine/isophthaloyl *trans*-2,5-dimethylpiperazine.

case, the maxima in the rate curves were used, as the rate constants because the rate curves exhibited no linear parts. Figure 9 illustrates Arrhenius-type plots for the random and block copolymers. The calculated activation energies vary between 59 and 61 kcal/mole for the random and block copolymers, respectively, and the frequency factors are between 1.5 and 3.1 × 10^{17} sec^{-1} (Table 1). These values may be compared with the previously reported (*1,2*) activation energies of 64 and 53 kcal/mole for poly(terephthaloyl *trans*-2,5-dimethylpiperazine) and poly(isophthaloyl *trans*-2,5-dimethylpiperazine), respectively. The maximum rates (Table 1) indicate that the random copolymers degrade two to four times faster than the block copolymers at similar temperatures.

The relative thermal stability in vacuum of the random and block

TABLE 1

Rates and Activation Energies for the Thermal Degradation of
Piperazine Copolyamides

Copolymer	Temp., °C	Max. rate, % sample/min	Activation energy, kcal/mole	Frequency factor, sec^{-1}
Random, 50/50[a]	419	3.20		
	411	1.93		
	401	1.05	59	3.1×10^{17}
	392	0.61		
	381	0.25		
Block, 50/50[a]	428	1.88		
	420	0.90		
	410	0.51	60	1.5×10^{17}
	401	0.29		
	391	0.16		
Random, 70/30[a]	438	3.68		
	412	0.72		
	406	0.40	61	2.5×10^{17}
	392	0.20		
Block, 70/30[a]	440	2.50		
	429	1.22		
	419	0.76	61	1.9×10^{17}
	411	0.42		
	401	0.20		

[a] Refers to mole % compositions of copolymers of terephthaloyl *trans*-2,5-dimethylpiperazine/isophthaloyl *trans*-2,5-dimethylpiperazine.

TABLE 2

Relative Thermal Stability in Vacuum of Piperazine Copolyamides

Polymer	Activation energy, kcal/mole	T_h, °C
Random 50/50[a]	59	414
Block 50/50[a]	60	427
Random 70/30[a]	61	430
Block 70/30[a]	61	436

[a] Refers to mole % compositions of copolymers of terephthaloyl *trans*-2,5-dimethylpiperazine/isophthaloyl *trans*-2,5-dimethylpiperazine.
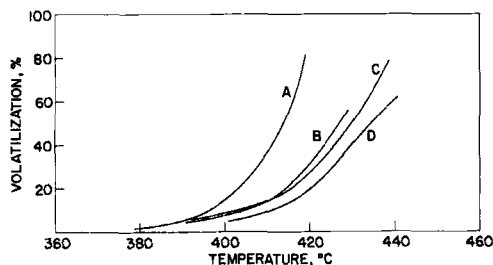
FIG. 10. Relative thermal stability in vacuum of piperazine copolyamides (isothermal heating for 30 min at various temperatures): A, 50/50 mole % random copolymer of t-2,5-DiMePip-T/and t-2,5-DiMePip-I; B, 50/50 mole % block copolymer of t-2,5-DiMePip-T/and t-2,5-DiMePip-I; C, 70/30 mole % random copolymer of t-2,5-DiMePip-T/and t-2,5-DiMePip-I; D, 70/30 mole % block copolymer of t-2,5-DiMePip-T/and t-2,5-DiMePip-I.

copolymers is illustrated in Fig. 10. This figure shows the percent volatilization as a function of temperature of pyrolysis between 380 and 440°C. Following the system of Madorsky (9), each curve was constructed from isothermal weight-loss experiments after the sample had been heated for 30 min at a given temperature (following a 15–20-min preheating period). It is apparent that the block copolymers (curves B and D) are more stable than the corresponding random copolymers (curves A and C). Table 2 shows the half-life (T_h) of the copolymers, which corresponds to 50% volatilization of the sample (9). It is apparent that the block copolymers have higher T_h values (and hence they are more stable) than the corresponding random copolymers with similar mole % composition.

Volatile Degradation Products

The results of the mass spectrometric analyses show that the volatile degradation products (Table 3) are generally similar to those of the corresponding homopolymers (1,2) and consist chiefly of carbon monoxide, carbon dioxide, ammonia, and methane, with smaller quantities of other components. The accuracy of the analysis of the major components is about ±10%, whereas that of the minor components is estimated to be ±20%. Water is probably not a true degradation product but is due to adsorbed moisture in the polymer. As had been pointed out previously, (1,2) the appearance of carbon monoxide in the pyrolysis products is unlike the situation

TABLE 3

Mass Spectrometric Analysis of Degradation Products Volatile at
Room Temperature of Piperazine Copolyamides during
Vacuum Pyrolysis
($475°C$, 1 hr, $\sim 10^{-5}$ mm Hg)

Component	Random 50/50,[a] mole %	Block 50/50,[a] mole %	Random 70/30,[a] mole %	Block 70/30,[a] mole %
Carbon monoxide	35.3	37.9	37.9	33.7
Carbon dioxide	14.7	14.2	10.3	8.5
Water	14.1	11.8	13.5	14.5
Ammonia	13.2	14.0	14.1	16.4
Hydrogen	0.7	0.7	0.9	Not determined
Nitrogen	4.5	0.1	1.1	0.4
Methane	7.0	8.1	7.1	13.3
Ethane	3.6	3.3	3.7	4.6
Propane	0.9	0.9	0.7	0.9
Acetone (?)	1.4	2.1	1.6	1.6
Pyrrole	0.7	0.8	1.1	0.1
Methylpyrrole	0.4	0.5	0.7	0.5
2-Methylpyrazine	0.5	0.8	1.0	0.9
Dimethylpyrazine	1.4	2.1	3.2	1.9
Benzene	1.2	1.9	1.8	1.7
Xylene	0.2	0.4	0.4	0.4
Benzonitrile	0.2	0.3	0.3	0.2
Methylbenzonitrile	<0.1	<0.1	0.1	<0.1
Benzoic acid	0.1	0.2	0.3	0.1

[a] Refers to mole % compositions of copolymers of terephthaloyl *trans*-2,5-dimethylpiperazine/isophthaloyl *trans*-2,5-dimethylpiperazine.

with aliphatic polyamides, where vacuum pyrolysis produces considerable quantities of carbon dioxide but only traces of carbon monoxide (7,8). The appearance of large amounts of carbon dioxide is attributed to hydrolytic processes (7,8) and less to branching and cross-linking reactions involving the end groups and the peptide linkages (10). As was the case with the homopolymers, the general character of the rate curves, high activation energies, and the composition of the volatile degradation products point to an essentially random degradative mechanism during pyrolysis in vacuum.

Electrical Properties. The dielectric properties of poly(terephthaloyl *trans*-2,5-dimethylpiperazine), poly(isophthaloyl *trans*-2,5-dimethylpiperazine), and their copolymers have been studied at

different relative humidities between 0.1 and 100 kcps. The data in Table 4 show that at the relative humidities of 0–4% and at 54–56%, the dielectric constants and the dissipation factors of the random and block copolymers, as well as the homopolymers, are almost

TABLE 4

Dielectric Constants (K) and Dissipation Factors (D) of Piperazine Copolyamides at 0–4% and 54–56% Relative Humidities

Sample	Frequency, kcps	0–4% RH		54–56% RH	
		K	D	K	D
Poly(t-2,5-DiMePip-I)	0.1	2.8	0.001	4.2	<0.001
	1	2.8	<0.001	4.2	<0.001
	10	2.8	0.001	4.2	0.001
	100	2.8	0.002	4.1	0.003
Poly(t-2,5-DiMePip-T)	0.1	2.7	<0.001	4.0	0.005
	1	2.7	<0.001	3.9	0.004
	10	2.7	<0.001	3.9	0.003
	100	2.6	<0.001	3.9	0.004
Block 70/30[a]	0.1	2.9	<0.001	4.5	0.003
	1	2.9	<0.001	4.4	0.001
	10	2.9	0.001	4.4	0.002
	100	2.9	0.001	4.4	0.004
Random 70/30[a]	0.1	2.8	<0.001	5.0	<0.001
	1	2.8	<0.001	5.0	0.001
	10	2.8	0.001	4.9	0.001
	100	2.9	0.002	4.9	0.004
Block 30/70[a]	0.1	2.9	<0.001	4.7	0.003
	1	2.9	<0.001	4.6	0.002
	10	2.8	0.001	4.6	0.002
	100	2.9	0.002	4.6	0.004
Random 30/70[a]	0.1	2.8	<0.001	4.6	0.004
	1	2.7	<0.001	4.6	0.003
	10	2.7	0.001	4.5	0.002
	100	2.7	0.002	4.5	0.005
Block 50/50[a]	0.1	2.8	<0.001	4.6	0.001
	1	2.8	<0.001	4.6	<0.001
	10	2.8	0.001	4.6	0.001
	100	2.7	0.002	4.4	0.002
Random 50/50[a]	0.1	2.5	<0.001	3.8	<0.001
	1	2.5	<0.001	3.8	<0.001
	10	2.5	<0.001	3.8	<0.001
	100	2.4	0.001	3.7	0.003

[a] Refers to mole % compositions of copolymers of terephthaloyl *trans*-2,5-dimethylpiperazine/isophthaloyl *trans*-2,5-dimethylpiperazine.
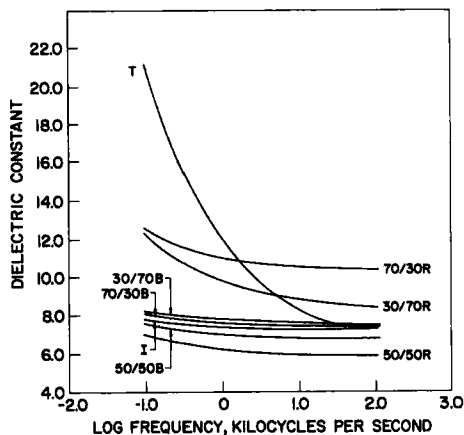
FIG. 11. Dependence of dielectric constants on frequency at 75–80% relative humidity for piperazine polyamides and their copolymers: T, poly(t-2,5-DiMePip-T); I, poly(t-2,5-DiMePip-I); B, block copolymer, T/I, in mole %; R, random copolymer, T/I in mole %.
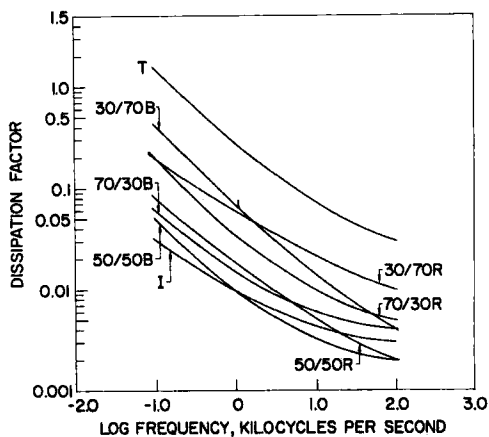

FIG. 12. Dependence of dissipation factor on frequency at 75–80% relative humidity of poly(terephthaloyl *trans*-2,5-dimethylpiperazine) and poly(iso-phthaloyl *trans*-2,5-dimethylpiperazine) and their copolymers: T, poly(t-2,5-DiMePip-T); I, poly(t-2,5-DiMePip-I); B, block copolymer, T/I in mole %; R, random copolymer, T/I in mole %.

independent of frequency and vary little from each other. On the other hand, at 75–80% relative humidity there are significant differences between these samples, as indicated by Figs. 11 and 12. Poly(terephthaloyl *trans*-2,5-dimethylpiperazine) shows a dielectric constant of 21 and a dissipation factor of 1.5 at 0.1 kcps, decreasing to 7.3 and 0.003, respectfully, at 100 kcps. Poly(isophthaloyl *trans*-2,5-dimethylpiperazine), on the other hand, does not exhibit such large changes. The pronounced frequency dependence of the dielectric properties of poly(terephthaloyl *trans*-2,5-dimethylpiperazine) at 75–80% relative humidity may be associated with hydrogen-bonded water and with the crystalline/amorphous structure of the polymer. The electrical properties of the 70/30 and the 30/70 mole % block copolymers are less frequency-dependent than the corresponding random copolymers.

Acknowledgments

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Zusammenfassung

Der thermische Abbau von statischen und Blockcopolymeren aus Terephtaloyl-*trans*-2,5-dimethylpiperazin/Isophtaloyl-*trans*-2,5-dimethylpiperazin wurden in Bezug auf Reaktionsgeschwindigkeiten, Aktivierungsenergien, Abbauprodukte, und elektrische Eigenschaften untersucht. Die Abbaugeschwindigkeiten und die Art der flüchtigen Abbauprodukte weisen darauf hin, dass beide Arten von Polymeren, die statistischen als

auch die Blockcopolymeren, im Vacuum nach einer Art radikalischen Spaltungsmechanismus in statistischer Weise reagieren, wobei Aktivierungsenergien von 59 bis 61 kcal erhalten wurden. Im Temperaturbereich von 390 bis 440° sind die Blockpolymeren marklich stabiler im Vacuum (die Geschwindigkeiten sind zwei bis vierfach langsamer) als die statistisch aufgebauten Copolymeren. Im Gegensatz zu den statistisch aufgebauten Copolymeren, zeigen die Blockpolymeren nur eine geringe Frequenzabhängigkeit ihrer Dielektrizitätskonstanten und Verlustfaktoren von 0.1 bis 100 kcps.

Résumé

On a étudié les vitesses, les énergies d'activation, les produits de dégradation, et les proprietés électriques de la dégradation thermique des copolymères désordonnés et sequencés de la terephthaloyl *trans*-diméthyl-2,5-piperazine/isophtaloyl *trans*-diméthyl-2,5-piperazine. Les vitesses de dégradation et la nature des produits volatiles indiquent que les copolymères désordonnés et sequencés obéissent le type radicalaire libre de dégradation presque désordonnée dans le vide, avec des énergies d'activation entre 59 et 61 kcal/mole. Dans l'intervalle de températures de 390 et 440°C les polymères sequencés sont beaucoup plus stables dans le vide (la vitesse de dégration est deux à quatre fois plus lente) que les polymères désordonnés. Contrairement aux copolymeres désordonnés les copolymères sequencés montrent une très légère dépendance de leurs constantes diélectriques de la fréquence. Leurs facteurs de dissipation ont des valeurs comprises entre 0.1 et 1.00 kcps.