

THERMALLY STABLE POLYMERS BASED ON BIS-ACENAPHTHYLS

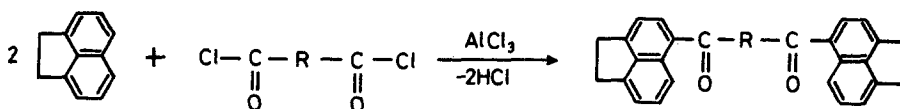
A. L. Rusanov, E. G. Bulycheva and S. S. Bocharov

A. N. NESMEYANOV INSTITUTE OF ELEMENTOORGANIC COMPOUNDS, USSR
ACADEMY OF SCIENCES, MOSCOW, USSR

The thermal stability of poly-bis-acenaphthyleneis was studied by dynamic and isothermal TG methods.

All these polymers demonstrate high thermal stabilities; increasing length of the dicarboxylic acid leads to an enhancement of the thermal properties of the polymers.

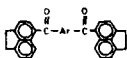
The development of the chemistry and technology of thermostable polymers and the production of materials based on them is considerably impeded by the limited availability of most monomers and, specifically, the "key" compounds used in the synthesis of various polyfunctional systems. Accordingly the use of a "key" compound, acenaphthene [1], a widely applied hydrocarbon, the content of which in coal tar reaches 1.5 % [1], is of considerable interest. The diversity of the various conversions of acenaphthene permits the prospect of the production of various compounds of use for the preparation of different condensation monomers. Of especially great interest among such compounds are the bis-acenaphthyls, obtained from acenaphthene and aromatic dicarboxylic acid dichlorides via the Friedel-Crafts reaction [2-6]:



Study of the dependences of the yields of the main bis-acenaphthyls on the catalyst nature and quantity, the solvent, the reagent mixing order, the temperature and the reaction duration revealed the optimal conditions for condensation: a reaction time of 4 hr at 0 to 60°, with tetrachloroethane as the solvent, and aluminium chloride as the catalyst. Under these conditions,

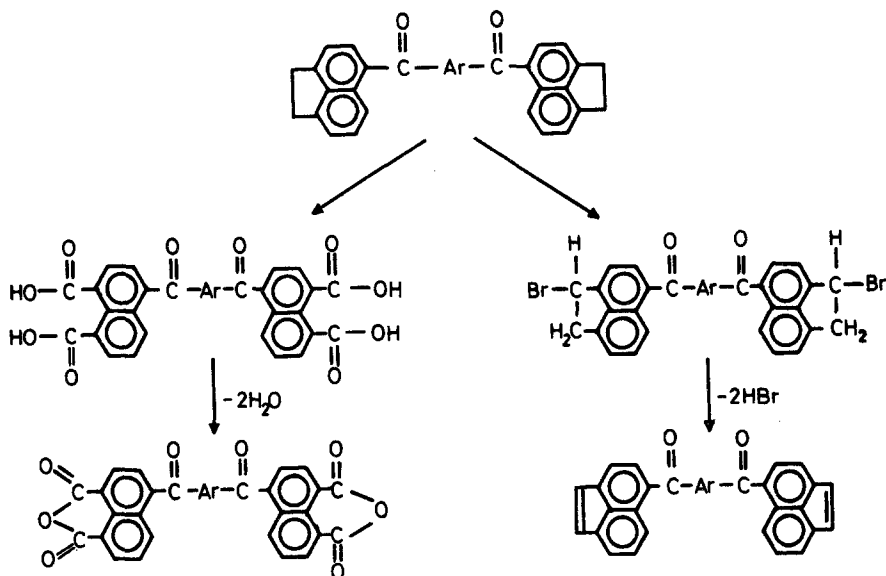
bis-acenaphthyls were obtained in yields of 80 to 96 %. The structures of these compounds were confirmed by elemental analysis (Table 1), and by IR and NMR spectroscopy. Their properties are given in Table 1.

Table 1 Some characteristics of aroylene-bis (acenaphth-4-yls) of the general formula



-Ar-	Melting point, °C	Elemental analysis Found/Calculated, %				Yield, %
		C	H	S	F	
	244-244.5	86.76 86.67	5.23 5.02			88
	189-190	87.37 87.67	5.15 5.02			86
	179-180	86.26 86.04	5.19 4.91			98
	181-182	86.26 86.35	4.91 4.80			85
	245-246.5	78.91 78.89	4.56 4.50	5.61 5.54		80.5
	175-176	74.27 74.08	3.89 3.94		16.95 17.15	96

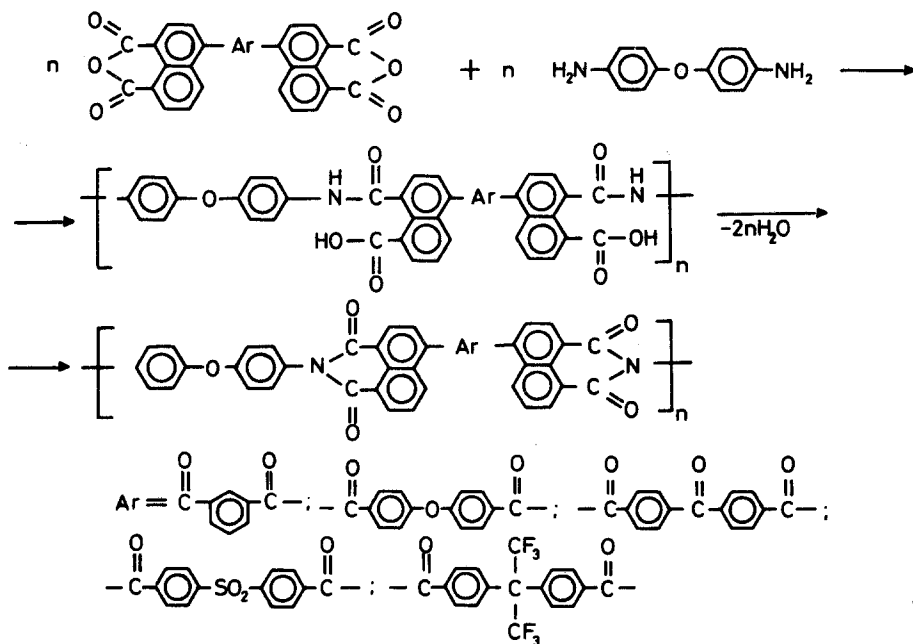
The bis-acenaphthyls thus obtained were converted to the corresponding bis(-naphthalic anhydrides) [2-5] and bis-acenaphthylenes [7-9] in accordance with the following scheme:



Bis(naphthalic anhydrides) were prepared via the oxidation of bis-acenaphthyls and dehydration of the tetracarboxylic acids thus obtained [2-5]. The bis-acenaphthyls were oxidized with sodium bichromate in acetic acid, potassium permanganate in pyridine, atmospheric oxygen in acetic acid, or nitric acid. On drying at 60 to 80° and 10 Torr, the oxidation products are in fact, bis(naphthalic anhydrides) rather than bis(naphthalic acids), due to the six-membered anhydride ring readily undergoing closure. The structures of the bis(naphthalic anhydrides) were confirmed by elemental analysis (Table 2) and IR spectroscopy; their properties are given in Table 2.

The syntheses of the bis-acenaphthylenes included bromination-dehydrobromination reactions. The first stages were carried out with N-bromosuccinimide, and the second stages with KOH in C₂H₅OH. The conversion of the bis-acenaphthyls to bis-acenaphthylenes was confirmed by ¹³C NMR and PMR methods.

The bis(naphthalic anhydrides) thus obtained were used for the preparation of different heterocyclic polymers. The simplest of these polymers (polynaphthylimides) were obtained by interaction of the bis(naphthalic anhydrides) with 4,4'-diaminodiphenyl ether:



Polynaphthylimides were in most cases synthesized under conditions of high-temperature polycondensation in *m*-cresol solution; benzoic acid was used as catalyst. Under these conditions, the intermediate poly(peri-carboxy)amide structures are practically not isolated, due to the decreased reactivity of the naphthalic anhydrides [10] and the easy formation of six-membered imide cycles [11].

Some characteristics of the synthesized polynaphthylimides are given in Table 3. They are soluble not only in sulfuric acid, but also in phenolic solvents. The comparatively low viscosity characteristics of these polymers can probably be improved significantly by selecting efficient catalytic systems.

The high softening temperatures of the polynaphthylimides and the generally known [11] increased hydrolytic stability of the naphthylimide cycles stimulate further research in this direction.

Considerably more attention by researchers, as compared with the polynaphthylimides, was attracted by the polynaphthylenebenzimidazoles. These systems were synthesized in accordance with the following general scheme [3-5, 12]:

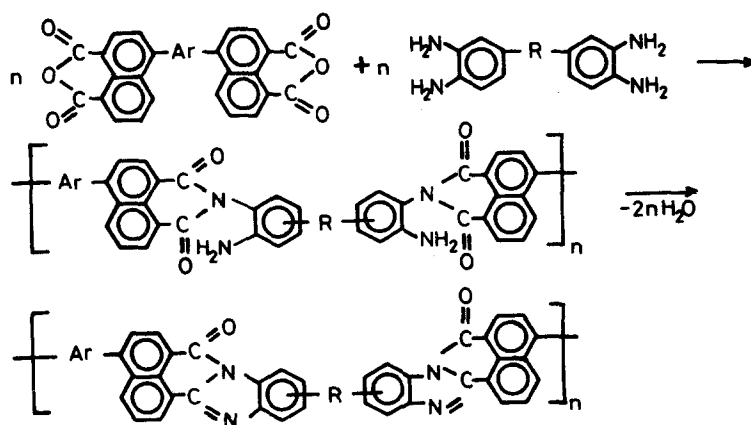
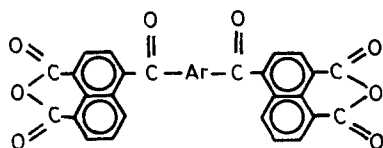

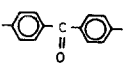
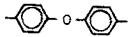
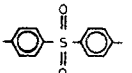
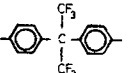


Table 2 Some characteristics of aroylene-bis (naphthalic anhydrides) of the general formula



-Ar-	Melting point, °C	Elemental analysis Found/Calculated, %				Yield, %
		C	H	S	F	
	>450	81.83 73.00	5.16 2.68			70.8
	434-436	72.40 73.00	2.97 2.61			90.2
	309-301	73.64	3.15			93.0
	313-314	73.72 74.28	2.87 2.87			94.0
	341-342.5	76.62 68.46	2.95 2.71	4.45 4.81		89.1
	288-290	65.48 65.43	2.46 2.41		15.10 15.14	96.0

Table 3 Some characteristics of polynaphthylimides of the general formula

-Ar-	η_{red} , dl/g 0.5% solution in H ₂ SO ₄	$T_{soft.}$, °C	T of 10% weight loss, °C TG, $\Delta t = 5$ deg/min	Solubility			
				H ₂ SO ₄	<i>m</i> -cresol	TCE : phenol = 3:1	TCL
	0.72	310	500	+	+	+	+/-
	0.53	300	515	+	+	+	+/-
	0.78	275	490	+	+	+	+/-
	0.78	335	520	+	+	+	+/-
	0.32	305	510	+	+	+	+

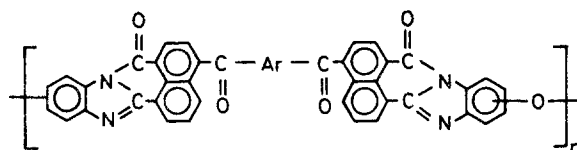
In spite of the fact that the best results (with respect to viscosities) were obtained in the syntheses of polynaphthoylenebenzimidazoles in *m*-cresol phosphate (*m*-cresol/P₂O₅) [13], most polymers were synthesized (on analogy with polynaphthylimides) in *m*-cresol medium with benzoid acid as a catalyst [3-5, 12]. Some characteristics of the synthesized polynaphthoylenebenzimidazoles are given in Table 4.

Analysis of the polynaphthoylenebenzimidazoles given in Table 4 indicates that, unlike their analogs obtained from naphthalene-1,4,5,8-tetracarboxylic acid [14, 15] as well as bis(naphthalic anhydrides) containing one ether, carbonyl and sulfone grouping each [16, 17], these polymers are soluble not only in strong acids, but also in phenolic solvents. The improved solubility of the systems given in Table 4 is probably a consequence of the increased number of simple bonds around which particular fragments of the macromolecular chains can rotate. On the other hand, by their solubility the

discussed polynaphthoylenebenzimidazoles exceed (qualitatively or quantitatively) the polynaphthylimides obtained from the same bis(naphthalic anhydrides). This is probably due to the presence in the polynaphthoylenebenzimidazoles of both a large set of isomers [18, 19] and "pyridine" nitrogen atoms, which determine the affinity of these systems for protogenic solvents [18, 19].

The polynaphthoylenebenzimidazoles given in Table 4 are characterized by the comparatively high viscosities of their solutions, with corresponding high molecular masses.

Table 4 Some characteristics of polynaphthoylene benzimidazoles of the general formula



-Ar-	η_{red} , dl/g H ₂ SO ₄	T_{soft} , °C	T of 10% weight loss, $\Delta t = 5$ deg/min °C	σ , kg/cm ²	ϵ , %	Solubility*		
						<i>m</i> -cre- sol	TCE : phenol 3:1	H ₂ SO ₄
	1.00	345	550	1260	15	+	+	+
	1.40	355	520	1100	13	+	+	+
	1.35	375	525	1000	11	+	+	+
	3.90	370	530	1040	11	+	+	+
	0.53	-	490	-	-	±	+	+
	1.80	360	545	1080	13	+	+	+

The higher viscosity and molecular mass characteristics of the polynaphthoethylenebenzimidazoles as compared with the polynaphthylimides can be explained specifically by the higher basicity and, therefore, the nucleophilicity of the bis(*o*-phenylenediamines) as compared with aromatic diamines containing the same "bridge" groups [20].

The thermal stabilities of the polynaphthoethylenebenzimidazoles obtained under conditions of dynamic and isothermal (Figs 1 and 2) thermogravimetric analyses were rather high. It appears evident that these polymers are characterized by the presence of considerable intervals between the temperatures of their softening and thermodegradation, which determines the possibility of their moulding. High-quality press-materials having excellent thermal and mechanical properties were obtained from some polynaphthoethylenebenzimidazoles. It should also be noted that films with acceptable mechanical properties (Table 4) were cast from solutions of the polynaphthoethylenebenzimidazoles in *m*-cresol.

The bis-acenaphthylenes attracted our attention [7-9] as thermosetting oligomers able to set, forming cross-linked structures without the release of low-molecular volatile by-products:

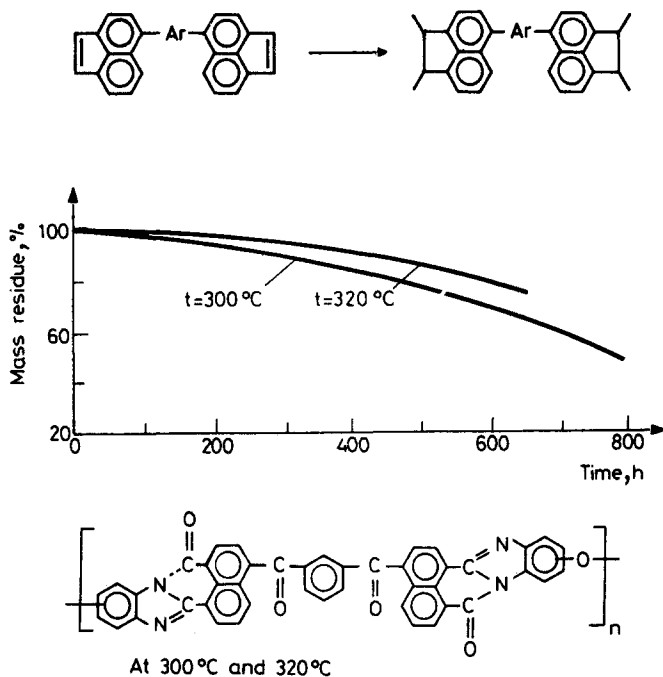


Fig. 1 Isothermal aging of polynaphthoethylenebenzimidazole

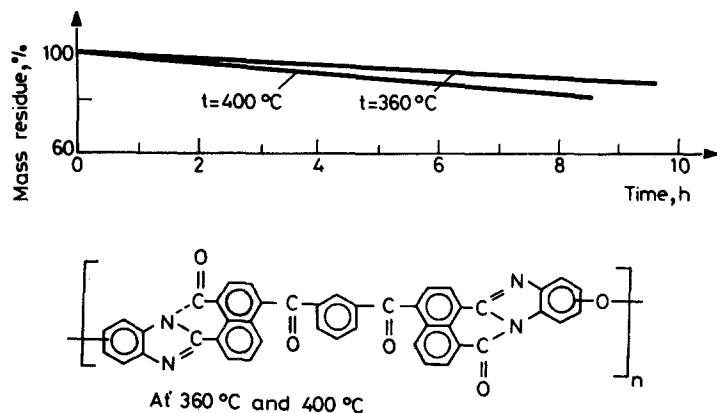
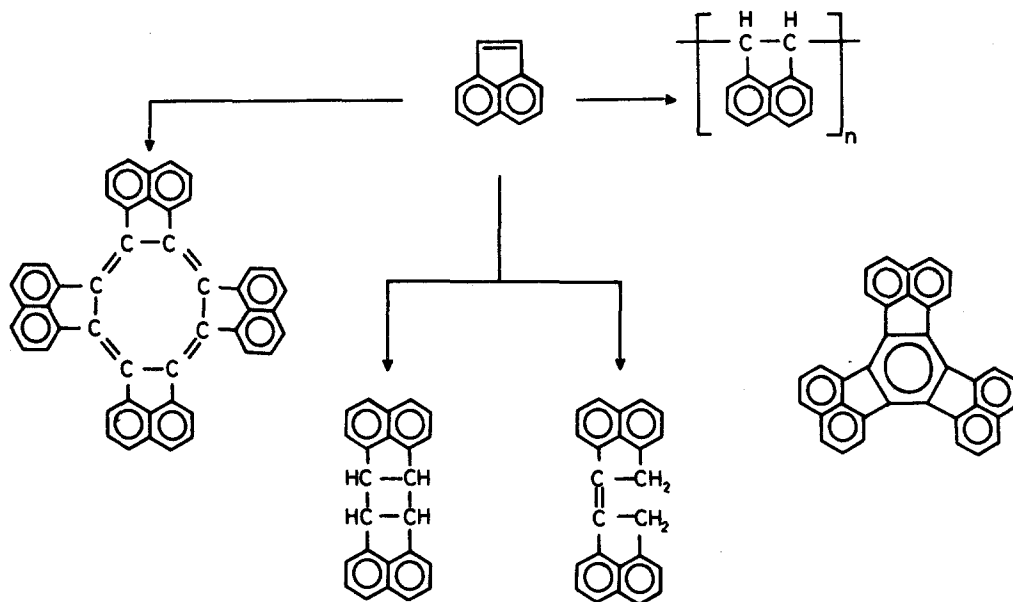


Fig. 2 Isothermal aging of polynaphthoylebenzimidazole

The by-systems are considered at present as some of the most promising binders for heat-resistant and thermostable composition materials [21]. An additional factor stimulating interest in the products of bis-acenaphthylene setting is the known ability of acenaphthylene to form condensed aromatic systems at high temperatures: fluoracyclene [22], diacenaphthylidene [22, 23] and heptacyclene [24].



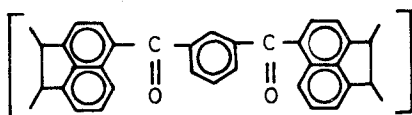
The formation of such system may lead to a significant improvement in the thermal characteristics of the end "three-dimensional" polymers.

DSC studies of the setting of bis-acenaphthylene based on the product of interaction of isophthaloyl chloride and acenaphthene and conforming to the formula

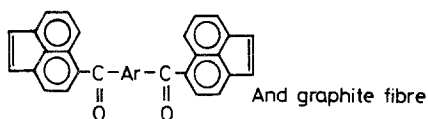


showed (Fig. 3) that the anomalies observed in the DSC curve within the region 155-210° are due to the processes of softening and polymerization of bis-acenaphthylene, whereas the exothermic peak at 300-360° (maximum at 330°) is associated with the formation of condensed systems. Therefore, three temperatures (240, 280 and 340°) were selected for moulding block samples. Some physico-mechanical characteristics of the polymers obtained are given in Table 5. It should further be noted that high-performance composites (reinforced with carbon fibre) were obtained from bis-acenaphthylenes (Table 6).

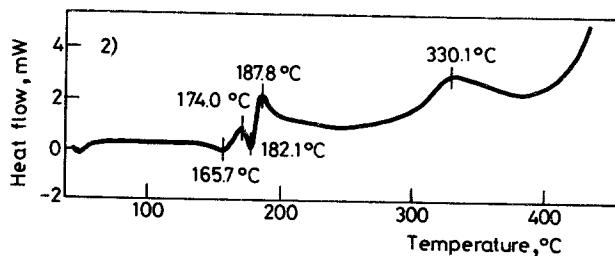
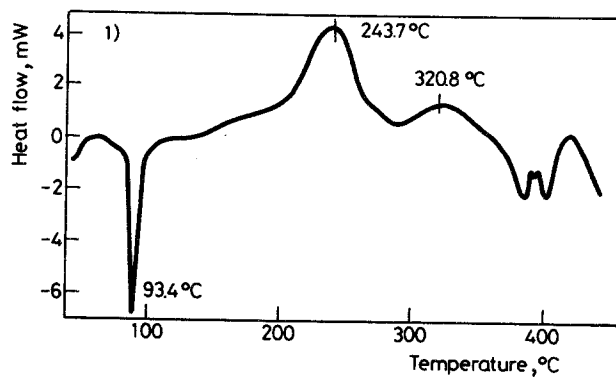
Table 5 Physico-mechanical characteristics of poly (bis-acenaphthylene)



Properties	Pressing temperature, °C		
	240	280	340
Specific impact strength A, kJ/m ²	1.0	1.3	0.6
Bending strength, b, MPa	12.4	24.5	15.0
Compression strength, c, MPa	130	130	110
Modulus of elasticity in compression, E c, MPa	2290	2250	1570

Table 6 General properties of composites prepared from bis-acenaphthylenes of general formula

-Ar-	Density, D, g/cm ³	Flexural strength, E _f , MPa	Flexural Modulus, E _f .10 ⁴ , MPa
	1.4 (20°C)	278 (20°C) 154 (290°C)	4.00 (20°C) 2.80 (290°C)
	1.4 (20°C)	493 (20°C) 368 (290°C)	
	1.4 (20°C)	395 (20°C) 234 (290°C)	

**Fig. 3** DSC curves of acenaphthylene (1) and bis-acenaphthylene (2)

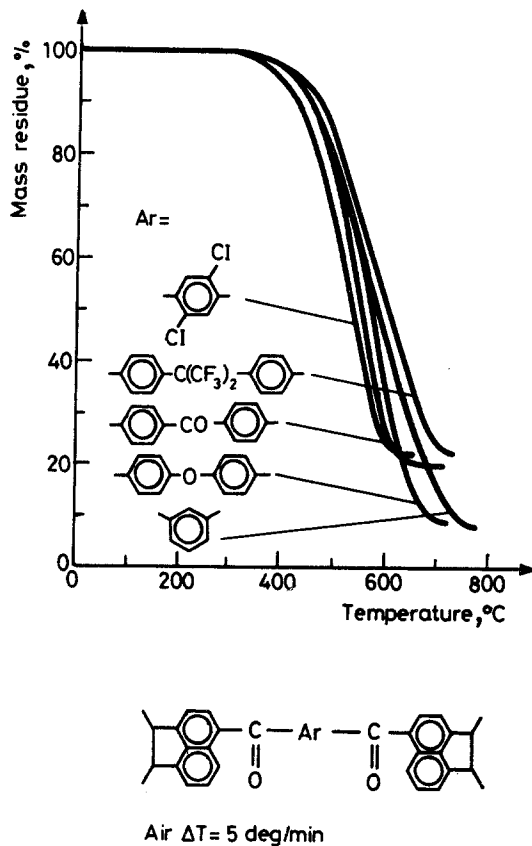


Fig. 4 Dynamic TG curves for polyacrylyene-bis-acenaphthylenes of general formula

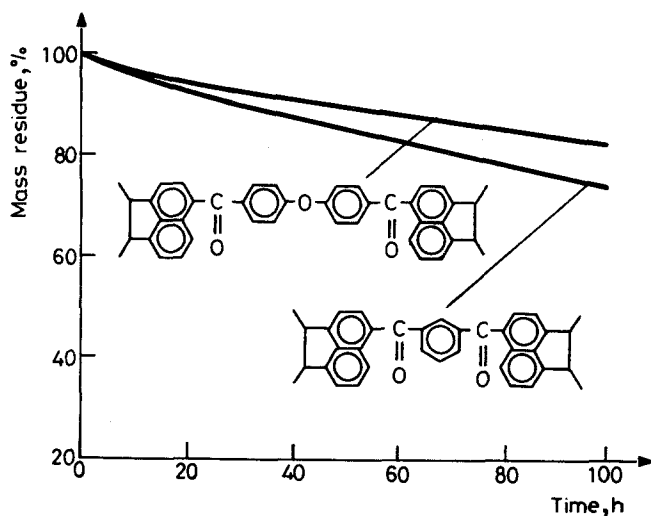


Fig. 5 Isothermal TG curves for poly-bis-acenaphthylenes (air, 300°C)

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Zusammenfassung — Mittels dynamischen und isothermischen TG-Methoden wurde die thermische Stabilität von Poly-bis-acenaphthylenen untersucht. Jeder dieser Polymere zeigt eine hohe thermische Stabilität; längere Dicarbonsäuren führen zu einer Verbesserung der thermischen Eigenschaften der Polymere.