Structure–property relationships in PMR-type polyimide resins: 1. Novel anthraquinone-based PMR resins*

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(Received 1 March 1993)

Novel aromatic polyimides prepared via the polymerization of monomeric reactants (PMR) approach and incorporating anthraquinone diamines in the main chain have been characterized. Imidization and crosslinking reaction profiles have been delineated by d.m.t.a. and the high-temperature mechanical and thermal properties of the thermoset resins examined. Elevated glass transition temperatures (>300°C) are apparent in some resins while impairment of mechanical integrity is not evident below 450°C. All resins show good thermal and thermo-oxidative stability.

(Keywords: anthraquinone polyimides; PMR; thermal stability)

INTRODUCTION

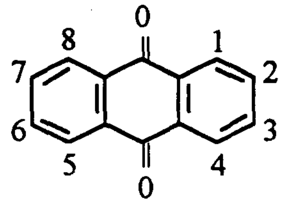
The NASA-developed polyimide, PMR-15 (*Figure 1*), is the leading matrix resin for composites intended for high-temperature aerospace applications. However, the PMR-15 resin system suffers several drawbacks, including microcracking during thermal cycling and possible monomer (MDA) toxicity[2]. In an attempt to develop alternative PMR monomers to improve resin characteristics, polyimides incorporating the anthraquinone moiety into the structure have been produced, as described in this report.

The inclusion of tricyclic fused ring structures such as anthraquinone in the polyimide backbone will produce short rod-like, dual strand (ladder) segments inherent to the polymer chain. This would be expected *a priori* to increase the mechanical rigidity and thermal stability of the resultant resin. This paper describes work directed towards the synthesis of novel oligomers containing anthraquinones and the characterization of the PMR pre-polymeric and polymeric formulations prepared therefrom.

EXPERIMENTAL

Materials

Benzophenonetetracarboxylic diacid-diester (BTDE) and nadic acid-ester (NE) were used as supplied by BP International plc. 1,4-Diaminoanthraquinone (1,4-AQ) and 2,6-diaminoanthraquinone (2,6-AQ) were obtained from Aldrich.



AQ structure

1,5-Diaminoanthraquinone (1,5-AQ), 1,5-diamino-4,8-dihydroxyanthraquinone (1,5-AQ-OH) and 1,8-diamino-4,5-dihydroxyanthraquinone (1,8-AQ-OH) were kindly donated by Dr P. Woolven (ICI Organics Division, Grangemouth, Stirlingshire, Scotland).

Synthesis

The PMR synthetic route, described elsewhere[1], and summarized in *Figure 1*, involves production of staged (oligomeric) prepolymers from a homogeneous monomer mixture followed by high temperature and pressure cure to form the crosslinked resin. In the current work, staged intermediates were prepared by heating a homogeneous mixture of monomers *in vacuo* at 70°C for 60 min, followed by 120 min at 135°C. The intermediates were then purified by Soxhlet extraction (to remove unreacted monomers) and dried to constant weight. Curing of the

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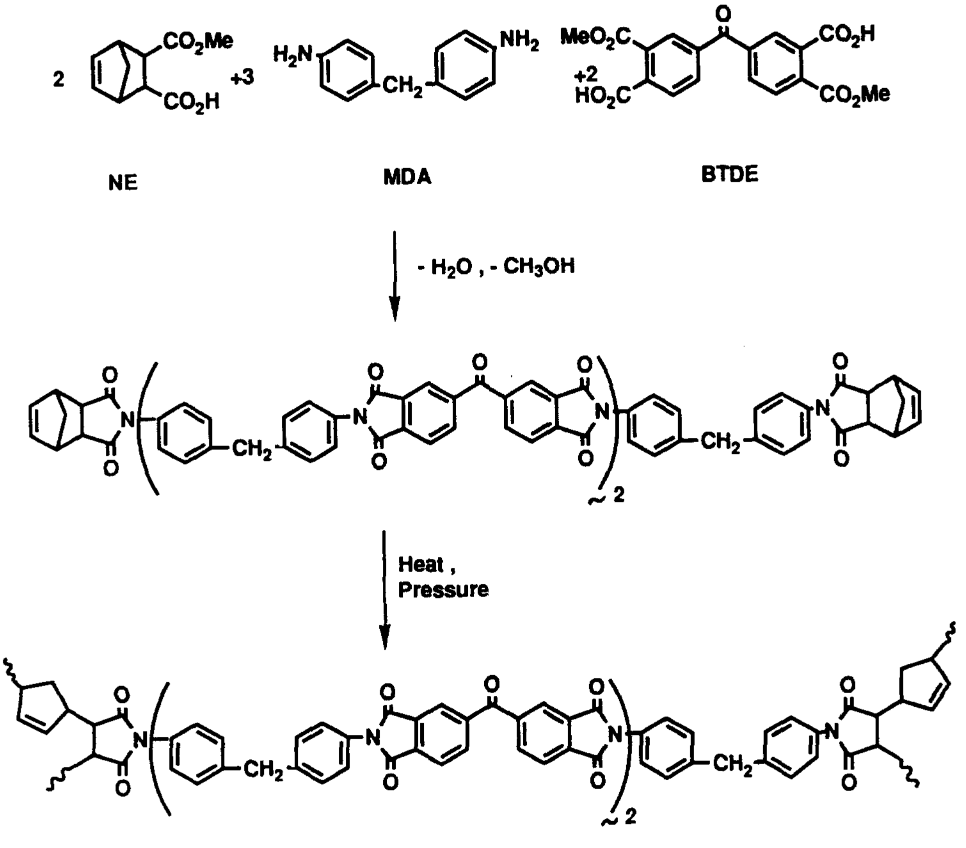

Figure 1 Synthesis of PMR-15

PMR resin was effected by heating the staged materials at 218°C for 50 min followed by 330°C for 240 min under nitrogen at a pressure of 20 atm in an autoclave. Following this cure cycle, the autoclave and contents were allowed to cool naturally to room temperature.

Techniques

Oligomer molecular-weight distributions were determined using a Waters GPC system incorporating an r.i. detector and employing 100 Å and 500 Å PL-gel columns in tandem to achieve chromatographic separation. THF constituted the mobile phase and molecular weight parameters are reported herein as polystyrene equivalents.

Thermogravimetric analyses of the cured resins were carried out in both air and nitrogen atmospheres in a Perkin-Elmer TGA7 instrument. A heating rate of 20°C min^{-1} was employed throughout.

Dynamic mechanical thermal analysis (d.m.t.a.) of both monomer-impregnated glass braids and cured resin-supported braids were obtained using a Polymer Laboratories DMTA unit operating at a frequency of 10 Hz and a heating rate of 5°C min^{-1}. Sample preparation involved impregnating glass braids with high-solids-content monomer solutions and evaporating off the solvent. Monomer braids were run without further alteration, whilst cured resin braids were subjected to standard synthetic route heating regimes prior to d.m.t.a. examination. Difficulties were often encountered in the production of high-quality impregnated glass braids arising from the lowered solubilities exhibited by the monomers relative to those of the conventional PMR-15 system and the poor wetting characteristics of solutions of high-solids-content.

Table 1 G.p.c. molecular weight parameters for the staged prepolymers

Diamine	M_n	M_w	PD
1,4-AQ	1136	1751	1.5
1,5-AQ	833	1356	1.6
2,6-AQ	1057	1603	1.5
1,5-AQ-OH	1396	6848	4.9
1,8-AQ-OH	782	1077	1.4

RESULTS AND DISCUSSION

Staging characteristics

Oligomer synthesis proceeded smoothly to yield highly coloured products displaying a similar variety of chemical compositions and chain lengths as observed for conventional PMR-15 oligomeric species[1]. Molecular weight parameters for these prepolymers are presented in *Table 1*. Fully imidized bisnadimide, NE–diamine–NE, was synthesized for each diamine and identified as present in the chromatograms of each of the relevant oligomeric mixtures.

Unusually, the 1,5-AQ-OH PMR formulation yielded a considerable quantity of material of greater hydrodynamic volume (and therefore of higher apparent molecular weight) at the oligomer stage than the analogous staged PMR materials based upon the other AQ derivatives.

The staging and crosslinking steps of the PMR synthetic route can be modelled by d.m.t.a. For the conventional PMR-15 formulation, subjection of monomer-impregnated braids to a programmed, constant heating rate simulation of a resin cure allows five distinct regions of thermomechanical behaviour to be identified[1]: in the lowest T region (< 100°C) the storage modulus, *E'*, falls as the material softens. MDA melts in this region and poly(amido-esters) form. The second temperature regime (~110–170°C) covers the range in which staging of PMR formulations is generally performed. As the temperature is increased, the combined effects of production of higher molar mass material accompanied by increased imidization, which serve to increase the observed *E'* of the matrix, are counterbalanced by the increasing fluidity of the oligomeric mixture. These competing processes produce a maximum in *E'* at about 170°C, beyond which the softening of the matrix dominates, resulting in a decrease in *E'* to produce the third thermally defined region of d.m.t.a. behaviour. The high-temperature end of this region is marked by a minimum in *E'* resultant upon the onset of resin cure. Reactive NE terminal species decompose to produce crosslinking of the medium (see *Figure 1*). The effect is to make the curing resin more rigid and a fourth regime of temperature dependence of *E'* evolves (generally at temperatures in excess of about 250°C). In the final temperature region, the form of the temperature dependence of the d.m.t.a. trace is dependent upon PMR stoichiometry[1] but reflects the influence, to varying degrees, of the effects of

(i) the glass transition of the polyimide matrix;

(ii) further crosslinking (consequent upon 'loosening' of the matrix via the occurrence of the glass transition, itself considerably suppressed by existing crosslinks in the polyimide matrix); and

(iii) degradation of the polymer matrix at temperatures in excess of 450°C.

The thermal profiles obtained in the current work show features which parallel those observed in the conventional PMR-15 system. Anthraquinone-containing formulations, however, display some unique characteristics (see *Figure 2*). Little stiffening occurs on imidization (at ~110–150°C). Consequently, the maximum in *E'*, which is usually a prominent intermediate feature between the onsets of the staging and curing processes in PMR-15 and other PMR-type systems, is of relatively minor significance in d.m.t.a. curves modelling the curing behaviour of the anthraquinone-based systems (see *Figure 2*). Substitution of the rigid anthraquinone ring system for the more flexible diphenylmethane nucleus of MDA might have been expected to produce a more dramatic increase in *E'*, upon staging, than is evident in the cure curves for PMR-15 itself. If anything, it is the subsequent thermal region, i.e. that characterized by a decrease in modulus as the staged oligomers soften (generally at temperatures >170°C), which might have been expected to have been most markedly affected by introduction of the rigid ring system. It may be that the rigidity of the AQ system inhibits chemical reactivity, particularly cyclization to the imide species, within the staging region. Whatever the reason, the overall result is that softening of the monomer mixture is followed by a broad 'trough' in *E'* until the onset of curing (which generally occurs at about 250°C). Other things considered, this might result in ready processability of such resins in the fabrication of composites.

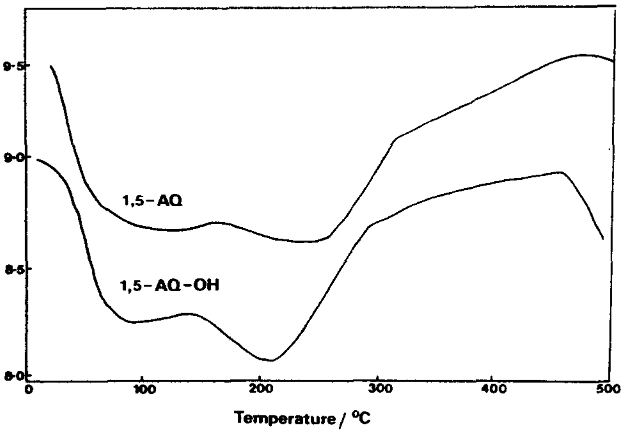

Figure 2 D.m.t.a. thermograms modelling the PMR synthetic route from monomer-impregnated braids containing 1,5-AQ and 1,5-AQ-OH

Table 2 Crosslinking onset temperatures (from d.m.t.a.)

Diamine	Onset temperature (°C)
1,4-AQ	254
1,5-AQ	249
2,6-AQ	252
1,5-AQ-OH	214
1,8-AQ-OH	266

Curing characteristics

Usually the reverse Diels–Alder (RDA) reaction and resultant modulus rise in d.m.t.a. thermograms due to crosslinking of the NE end-cap species is evident at temperatures in the region of 250°C (see *Figure 2* and *Table 2*). Anomalously in this series, 1,5-AQ-OH exhibits an onset temperature of about 215°C for the RDA process (see *Figure 2*). It is clear that the position and type of substitution in AQ-based diamines is crucial in influencing the rate of end-cap fragmentation. We intend to extend this work to a wider range of substituted AQs.

The crosslinking process appears to continue to higher temperatures than for PMR-15[1]. This feature is common to all AQ systems: the initial steep rise in modulus observed between 250 and 350°C moderates substantially at higher temperatures but only ceases with the onset of degradation (which leads to loss of rigidity) at temperatures in excess of 450°C.

Cured NE–diamine–NE resins

These materials show no change in modulus with increasing temperature until high temperature degradation (above 400°C) results in loss of mechanical integrity and falling modulus. This is in contrast to the behaviour of the cured resin derived from the bisnadimide NE–MDA–NE. This bisnadimide is an important oligomeric constituent contributing to the ultimate PMR-15 resin and evinces a glass transition temperature of 412°C in crosslinked form. Compared to MDA, the comparative rigidity of the AQ structural unit would lead to an elevation of the glass transition temperature of the AQ bisnadimide resins relative to that of NE–MDA–NE resin. It is probable, therefore, that the T_g is masked in the case of the AQ bisnadimide resins by the effects of the incipient degradation evident at such high temperatures. Alternatively, differences in chain rigidity and degrees of crosslinking may result, in the case of the AQ resins, in complete suppression of segmental movement in the network and thence of the transition which would result from such motions.

Cured PMR formulations

Glass transitions are apparent only for resins derived from 1,4-AQ (T_g=366°C) and 1,5-AQ (T_g=333°C) and, even in these resins, are highly suppressed (*Figure 3*). No glass transitions are apparent for the other formulations (*Table 3*). Suppression of the glass transition is resultant upon the rigidity imparted to the resin by incorporation of AQ units in the polymer backbone. Inclusion of 1,4-AQ results in a particularly high T_g value, the 1,4-AQ representing a pseudo *para*-phenylene diamine-type structure.

Lack of a glass transition for the 2,6-AQ derived resin seems initially somewhat surprising. Confirmation of this feature through examination of literature data on the T_g values of comparable structures, however, is restricted by lack of work in this area. No data have been reported on any thermoset polyimides containing anthraquinone diamines, nor on linear polyimides containing anthraquinone diamines with benzophenonetetracarboxylic dianhydride (BTDA). However, studies of linear polyimides prepared from 2,6-AQ and 1,4,5,8-naphthalene dianhydride[3] or 2,3,6,7-anthraquinone dianhydride[4] failed to detect a glass transition, concordant with our observations on the 2,6-AQ PMR system. There is some evidence for the presence of crystallinity in this sample (the melt endotherm is difficult to identify unambiguously in d.s.c., being close in temperature to the onset of degradation). If present, this would both suppress the effect of, and raise the temperature of, the glass transition.

For those resins in which a glass transition is in evidence, the stiffening effect of the anthraquinone unit is evident from comparison of the data in *Table 3* with the T_g values for analogous open-chain diaminobenzophenones (DABP)[5]. Values range from 259°C (*o,m'*-DABP + BTDA) to 293°C (*p,p'*-DABP + BTDA) for the open-chain diamines, in contrast to 333 and 366°C (*Table 3*) for anthraquinone diamines. Similarly, the linear polyimide prepared from 2,7-diaminofluorenone[6] (a stucturally related diamine) and BTDA exhibits a T_g of 347°C, further establishing the stiffening effect of incorporating fused tricyclic entities into the macromolecular backbone.

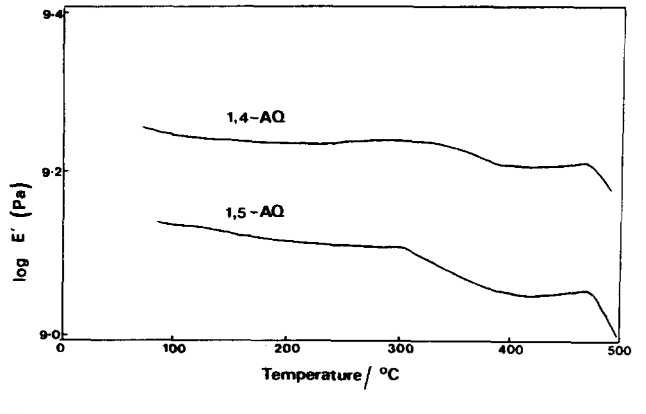

Figure 3 D.m.t.a. thermograms of cured resin braids containing 1,4-AQ and 1,5-AQ

Table 3 Effect of diamine structure on the physical properties of the cured resins

Diamine	T_g (°C) E'(onset)	T_g (°C) E'(1/2)	T_g (°C) E''(max)	High T crosslink	T(deg)[a] onset (°C)
1,4-AQ	309	370	366	v. small	467
1,5-AQ	309	342	333	v. small	473
2,6-AQ	Glass transition not apparent			[b]	470
1,5-AQ-OH	Glass transition not apparent			[b]	440
1,8-AQ-OH	Glass transition not apparent			[b]	443

[a] Onset of degradation of mechanical integrity
[b] Crosslinking not apparent

Table 4 Thermal and thermo-oxidative stabilities of cured resins in air and nitrogen atmospheres

Diamine	Nitrogen T(°C) for 5% wt loss	Nitrogen T(°C) for 10% wt loss	Air T(°C) for 5% wt loss	Air T(°C) for 10% wt loss
1,4-AQ	359	457	362	524
1,5-AQ	346	470	335	504
2,6-AQ	383	426	392	425
1,5-AQ-OH	364	383	357	393
1,8-AQ-OH	348	392	401	421

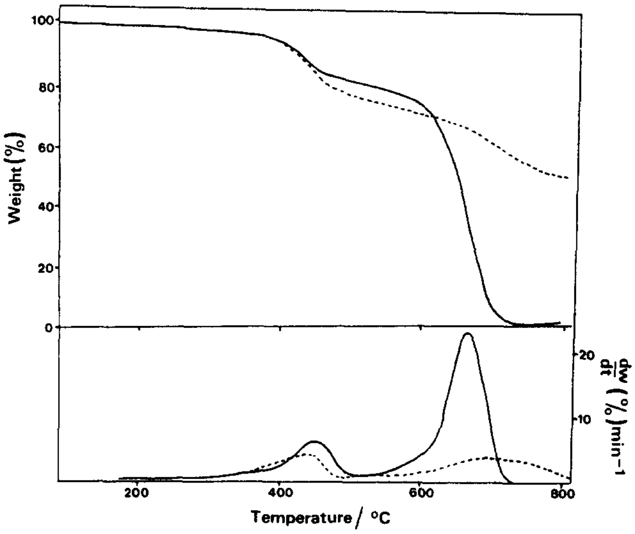

Figure 4 Thermogravimetric behaviour of cured 2,6-AQ resin in different environments; (——) air, (- - -) nitrogen

The classical PMR-15 formulation (and a variety of resins based on other structural variants) shows an additional cure process at high temperature released by the matrix mobility following the glass transition[1]. Such high-temperature modulus enhancement is essentially absent in the AQ systems (see *Table 3*).

The high-temperature mechanical performance of the resins is adversely affected by the presence of hydroxy substituents. For example, the onset of modulus decrease as a result of degradative processes is lowered from about 470°C for 1,5-AQ to about 440°C for 1,5-AQ-OH.

Thermogravimetric analysis

All resins show good thermal and thermo-oxidative stabilities (see *Table 4*). Degradation and accompanying weight loss is centred in two discrete temperature regions (see *Figure 4*). The relative importance of each temperature-dependent degradative mode, and the extent of the temperature window during which major weight loss occurs, is dependent both on the nature of the diamine structure incorporated within the macromolecular backbone and on the environment in which the degradative processes occur.

Initially, the *apparent* stability (as gauged by weight loss) is greater in air than nitrogen for all resin formulations. This has been observed in previous studies[1,7] of PMR resins. The lower weight loss under oxidative conditions can be attributed to oxygen uptake, forming peroxide and other species in the polymer matrix[8,9], during the lower temperature degradation region. At higher temperatures, however, thermo-oxidative processes result in enhanced degradation relative to that experienced in a nitrogen atmosphere. The overall relative stability trends for oxidative and non-oxidative conditions are indicated below.

Air 1,5-AQ-OH <2,6-AQ <1,8-AQ-OH <1,5-AQ <1,4-AQ

N_2 1,5-AQ-OH <1,8-AQ-OH ~ 2,6-AQ <1,5-AQ ~ 1,4-AQ

The introduction of hydroxy substituents to the anthraquinone structure leads generally to lowered thermal and thermo-oxidative stabilities, and it is our intention to evaluate the effects of other functional groups in this respect. Resins incorporating 1,8-AQ-OH are more stable than those based upon 1,5-AQ-OH both in air and nitrogen.

In the absence of hydroxy substituents, the AQ-based resins show interesting differences in stability. Resins incorporating 1,4-AQ and 1,5-AQ are inherently more inert than those based upon 2,6-AQ. Resins derived from 1,4-AQ would be expected to possess high stability, partly due to the pseudo *para*-phenylene diamine-type structure it represents. Resins of this type are known to exhibit high thermal stabilities even in comparison with those of resins derived from other related tricyclic diamines such as diaminofluorene[10,11] or diaminofluorenone[11]. 1,5-AQ, however, possesses an 'adjacent' isomeric structure to 2,6-AQ and yet exhibits higher resin stability.

Mechanistically, if cleavage of imide C–N or C–C bonds initiates polyimide breakdown[8,9], deactivation of the imide ring will lead to enhanced polymer stability. The presence of a neighbouring *para*-benzoquinone structure as a strong electron-withdrawing group results in deactivation of the imide ring[12,13]. Such a group is present as the central portion of all the anthraquinone diamines. In 1,5-AQ (and 1,4-AQ) the quinone unit is β to the nitrogen whereas in 2,6-AQ it is γ to the nitrogen. The deactivating influence is thus further removed in the case of the 2,6-AQ imide. Therefore, it will be less efficient in stabilizing the 2,6-AQ derived polymer as compared to the 1,5-AQ (and 1,4-AQ) derived polymers resulting in the observed enhanced thermal resilience of the latter resin.

CONCLUSIONS

New thermoset polyimides have been synthesized based on five anthraquinone diamines and benzophenonetetracarboxylic dianhydride. All resins showed good thermal and thermo-oxidative stabilities. In those resins in which a glass transition could be detected (containing 1,4- and 1,5-AQs), the value of T_g was higher than that of conventional PMR-15 resins. Resins derived from anthraquinone diamines bearing hydroxy substituents exhibited reduced stability with respect to thermal degradative processes.

ACKNOWLEDGEMENTS

The work reported forms part of a tripartite research project involving Lancaster University, Heriot-Watt University and BP plc. The permission of BP plc to publish this manuscript is gratefully acknowledged.

REFERENCES

1 Preston, P. N., Soutar, I., Woodfine, B. and Hay, J. N. *High Perf. Polym.* 1989, **1**, 161
2 Wilson, D. *Br. Polym. J.* 1988, **20**, 405
3 Browning, C. E. *US Patent 3 705 875* 12 December, 1972
4 Browning, C. E. *US Patent 3 702 318* 7 November, 1972
5 Bell, V. L., Stump, B. L. and Gager, H. *J. Polym. Sci., Polym. Chem. Ed.* 1976, **14**, 2275
6 Bell, V. L. *J. Polym. Sci., Polym. Chem. Ed.* 1976, **14**, 225
7 Hay, J. N., Preston, P. N., Soutar, I. and Woodfine, B. Eur. Tech. Symp. Polyimides, Montpellier, May 1989, A-4
8 Kovarskaya, B. M., Annenkova, N. G., Guryanova, V. V. and Blumenfeld, A. B. *Vysokomol. Soedin.* 1973, **A15**, 2458
9 Scala, L. and Hickam, W. *J. Appl. Polym. Sci.* 1965, **9**, 254
10 Dine-Hart, R. A. and Wright, W. W. *Makromol. Chem.* 1972, **153**, 237
11 Jewell, R. A. *J. Appl. Polym. Sci.* 1971, **15**, 1717
12 Delbig, H. and Plachky, M. *Angew. Makromol. Chem.* 1973, **31**, 75
13 Browning, C. E. *Am. Chem. Soc., Div. Org. Coat. Plast. Chem., Prepr.* 1970, **30**, 175