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DIELS-ALDER POLYMERIZATION OF AB-MONOMERS CONTAINING BENZOCYCLOBUTENE AND ALKYNE UNITS

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A novel class of aromatic imide AB-monomers with benzocyclobutene and an alkyne (primarily phenylethynyl group) as the reactive units have been prepared. The monomers have been utilized in the thermally induced Diels-Alder polymerizations. The differential scanning calorimetric study of the aforementioned AB-monomers provided two observations: (1) primary acetylene began its homo-polymerization (202°C max.) before the electrocyclic ring-opening of benzocyclobutene (270°C max.) (2) the phenoxy group connecting between phenylacetylenyl group and the aromatic imide fragment suppressed polymerization in Diels Alder fashion. Furthermore, thermoxidative stability evaluation on the cured samples (250°C for 8 hrs and then 350°C for another 8 hrs, under N_2 atmosphere), carried out at 650°F (air) for 200 hrs, indicated the more rigid phenylethynyl phthalimide system was the most heat-resistant.

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Block 11 (Continued)

Containing Benzocyclobutene and Alkyne Units

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work initiated under Project No. 2303, "Research to Define the Structure Property Relationships," Task No. 23Q303, Work Unit Directive 2303Q307, "Structural Resins." It was administered under the direction of the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr T. E. Helminiak as the ML Project Scientist. Co-authors were Dr F. E. Arnold, Materials Laboratory (AFWAL/MLBP) and Loon-Seng Tan, University of Dayton Research Institute.

This report covers research conducted from September 1984-March 1986. The authors wish to thank Edward Soloski, Marlene Houtz and Dr Ivan Goldfarb for their contributions in the termal analysis. The mass spectroscopic characterizations were performed Dr Chi K. Yu. A sample of bis(phenylacetylene) terminated monomer, 1 was kindly provided by Marilyn Unroe.

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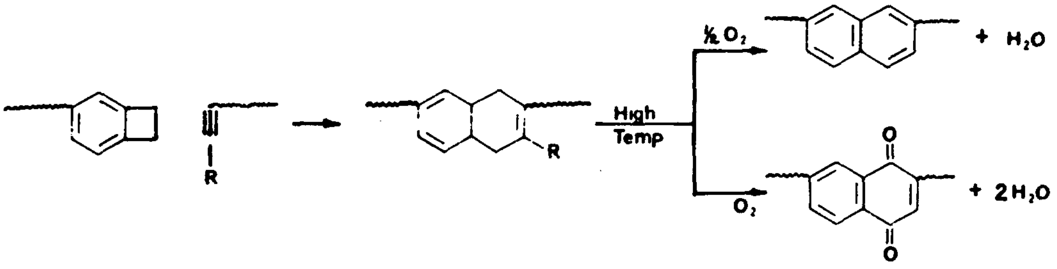
SECTION I

INTRODUCTION

The Diels-Alder reaction is a synthetically useful [4+2] cycloaddition reaction, in which an unsaturated group, that is a dienophile, combines with a 1,3-diene in a concerted fashion to form a six-membered ring. Whereas it is employed frequently in the constructions of complex organic molecules, it is less commonly utilized as a polymerization reaction [1-4]. Furthermore, only formally bifunctional dienes have been used. Hence, to exploit the reactivity of o-xylylene (or o-quinodimethane) as a powerful diene, generated in situ under thermal conditions from benzocyclobutene[5], we are presently investigating the synthetic utility of Diels-Alder reaction in polymerization chemistry with various combinations of benzocyclobutene and a number of dienophiles. Benzocyclobutene is thermally converted to a o-xylylene at approximately 250°C. The dienophile selected must exhibit stability up to the in situ generation of o-xylylene. Work in our laboratory on secondary acetylenes has shown[6] that they are stable to approximately 350°C, whereupon they react to form a conjugated polyene. Alkynes are also attractive because of the ease at which the structure derived from the cycloaddition can be transformed to a system with improved thermoxidative stability. Two such transformations are possible: (1) aromatization and (2) formation of benzoquinone:

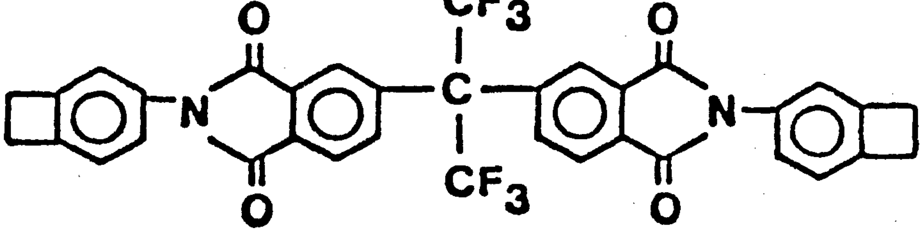


This report describes our work on the synthesis and characterization of a series of AB monomers containing alkyne and benzocyclobutene functionalities which polymerize via the Diels-Alder reaction.

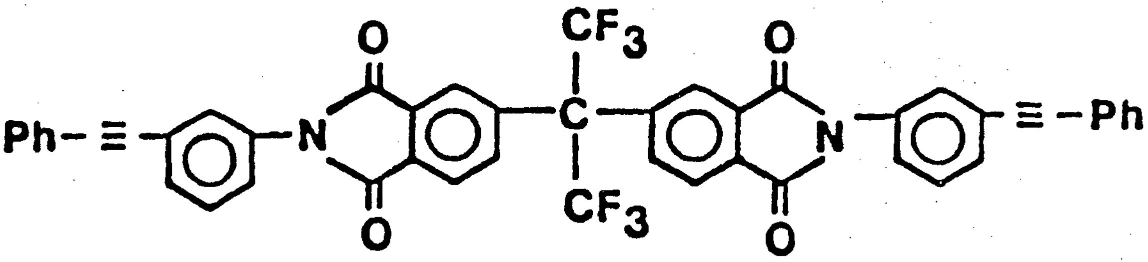
SECTION II

RESULTS AND DISCUSSION

Initially, we prepared a 1:1 stoichiometric mixture of the bis(benzocyclobutene) terminated monomer, 1 and the bis(phenylacetylene) terminated monomer, 2 by dissolving completely the components in methylene chloride. After the solvent had been removed by slow evaporation, the resultant mixture was dried in a vacuum-oven at about 70°C overnight.



1



2

The differential scanning calorimetric (DSC) study of the mixture exhibited a single glass-transition temperature at 95.6°C, indicating the compatibility of the mixture. However, it also depicted two reaction exotherms (See Figure 1). The larger exotherm with the maximum at 267.5°

can be attributed to the thermal reaction associated with the benzocyclobutene units and the smaller one is characteristically due to the homopolymerization of the phenylacetylene groups. The relative sizes of the reaction exotherms suggest that there is very little Diels-Alder polymerization occurring between 1 and 2. As a result, we proceeded to prepare a variety of AB monomers in an attempt to overcome the incomplete Diels-Alder polymerization in the aforementioned AABB system.

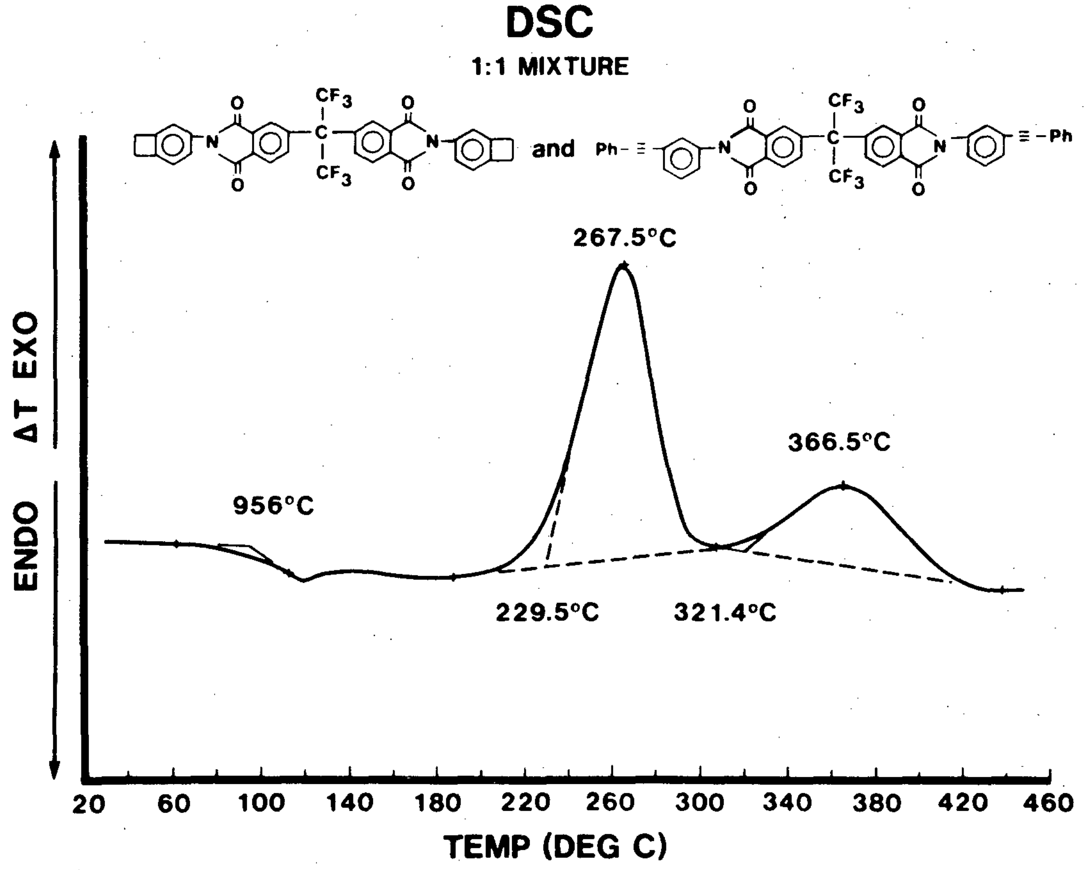
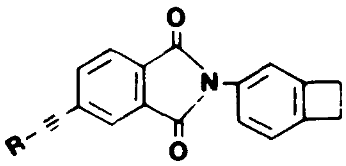


Figure 1. DSC thermogram of the compatible mixture (1:1 molar ratio) of bis(benzocyclobutene) terminated and bis(phenylacetylene) terminated monomers.

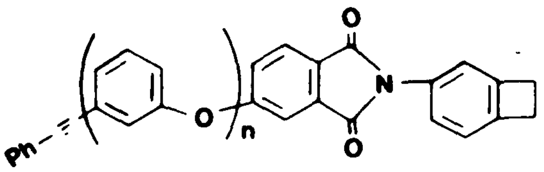
1. Synthesis

A novel class of aromatic imide AB-monomers with benzocyclobutene and an alkyne (primarily phenylethynyl group) as the reactive units have been prepared. The monomers have been utilized in the thermally induced Diels-Alder polymerizations. Three different types of backbone structures are shown below:



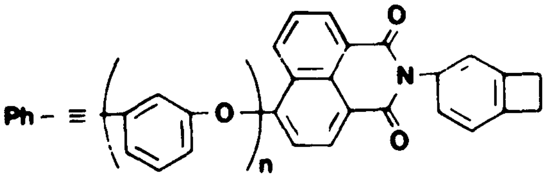
I

R=H, Ph, Me_3Si-



II

n=1,2

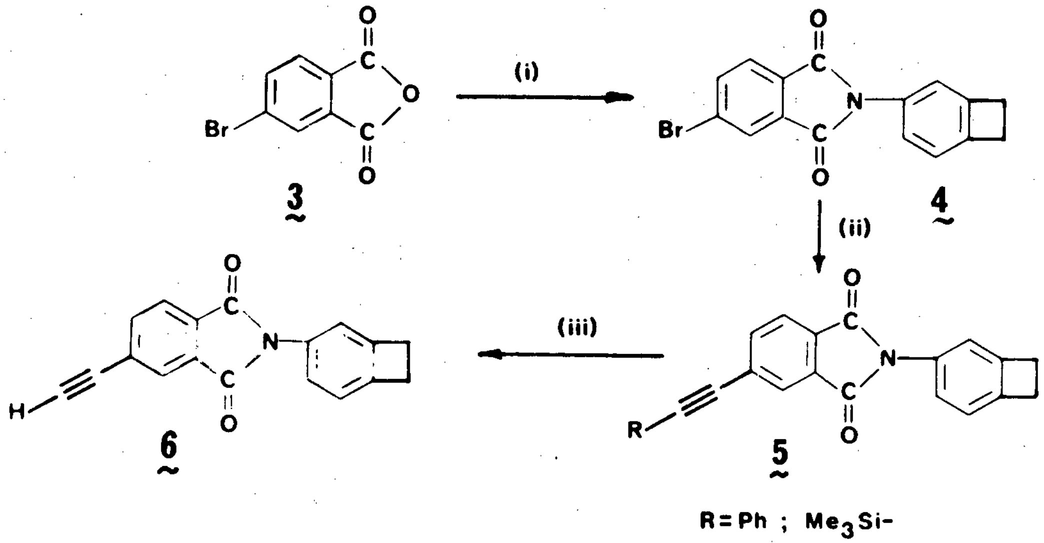


III

n=1,2

The preparation of 4-aminobenzocyclobutene <u>3</u>, was carried out according to the modified procedures adapted from the literature and was described in the preceding article. In brevity, the synthesis of the AB-monomers are as follows. Refluxing 4-bromophthalic anhydride in the presence of 4-aminobenzocyclobutene in glacial acetic acid under nitrogen for 17 hours led to the isolation of 4-bromo-(N-4-benzocyclobutenyl) phthalimide 4, in about 65-percent yield. Slightly improved yield may be achieved by utilizing a Dean-Stark trap to remove the water of imidization azeotropically with toluene. Ethynylation of the phthalimide 4 with either phenylacetylene or trimethylsilylacetylene, using palladium acetate and triphenylphosphine as the catalytic system, and triethylamine as both the solvent and hydrogen bromide scavenger [7] resulted in the desired alkyne-benzocyclobutene phthalic imides, (5a, R=Ph; 5b R=Me_3Si) in quantitative yields. The primary acetylene-benzocyclobutene phthalimide was prepared by stirring a mixture of potassium carbonate and the corresponding trimethylsilylacetylene, 5b, in methanol at room temperature according to the procedure described by Lau and co-workers[7]. (See Scheme I.)

SCHEME I



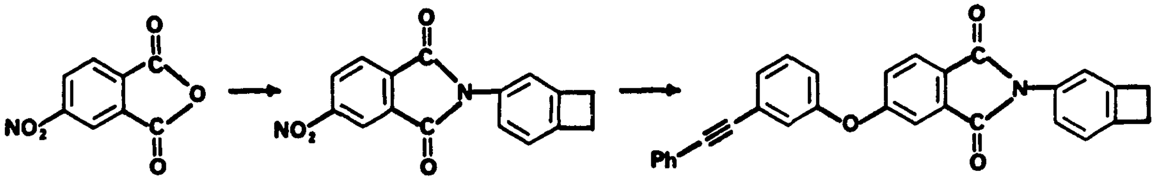
(i) 4-AMINOBENZOCYCLOBUTENE, CH_3CO_2H, REFLUX, N_2, 17 HRS (70%)

(ii) R-C≡CH, $Pd(OAc)_2$, PPh_3, NEt_3, N_2, 100° C, 3 HRS (87-95%)

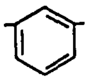
(iii) K_2CO_3, MeOH, N_2, r.t. (90%)

The remaining two AB-monomers were prepared similarly as outlined in Schemes II and III. Their synthesis involved the displacement of the nitro-groups from the imide intermediates, 8 and 11 by the potassium salt of 3-hydroxtolane 15 in DMSO. The phthalimide, 8, and naphthalimide, 11, were obtained from the reaction of 4-nitrophthalic anhydride 7 or 4-nitronaphthalic anhydride and 4-aminobenzocyclobutene under standard conditions. The preparation of 3-hydroxytolane 15 is depicted in Scheme IV. Direct ethynylation of 3-bromophenol with phenylacetylene using the usual catalytic system, Pd $(OAc)_2/PPh_3/NEt_3$, was attempted unsuccessfully. However, when the hydroxyl group was protected by a trimethylsilyl group and using tri-o-tolylphosphine instead of triphenylphosphine in the catalytic system[8], 15 was obtained in good yield. Since the trimethylsilyl group can be removed during work-up using $MeOH/H_2O$, it proves to be a useful protecting group for ethynylation of substrate containing the hydroxyl group.

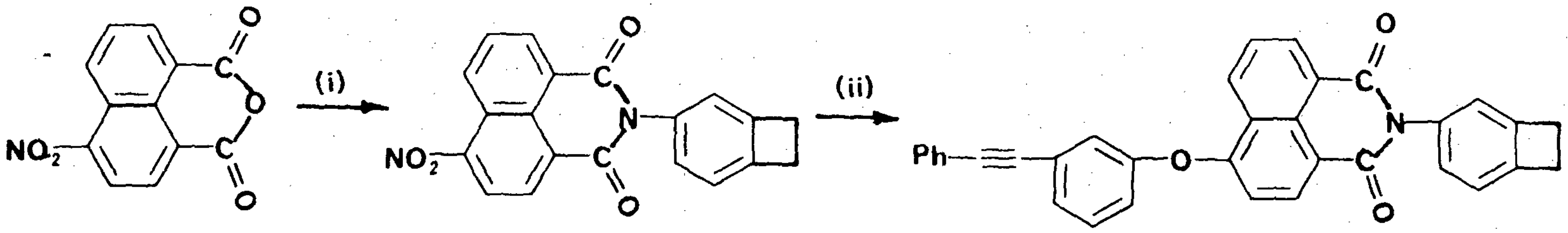
SCHEME II



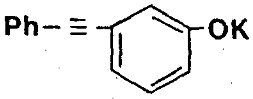
(i) 4-AMINOBENZOCYCLOBUTENE, CH_3CO_2H, REFLUX, N_2, 17 HRS

(ii) Ph-≡--OK , DMSO, r.t. N_2

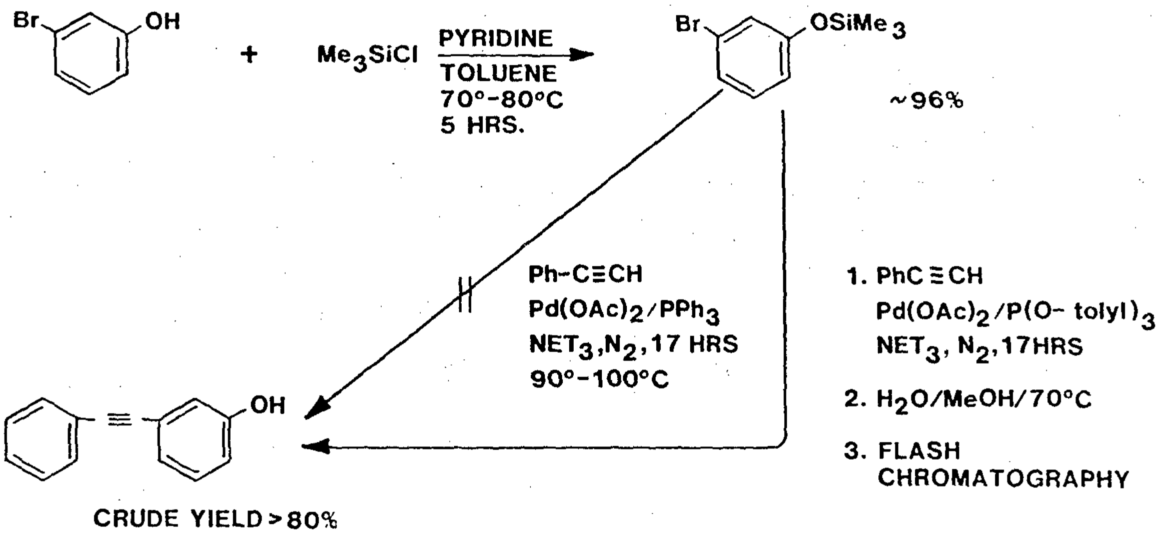
SCHEME III



(i) 4-AMINOBENZOCYCLOBUTENE, CH_3CO_2H, REFLUX, N_2, 17 HRS

(ii)  , DMSO, r.t. N_2

SCHEME IV



2. Characterization

The thermal characteristics and thermo-oxidative stabilities of the AB-(benzocyclobutene/alkyne) monomers and the corresponding thermosetting resins were determined by differential scanning calorimetry (DSC) and thermomechanical analysis (TMA). Isothermal gravimetric analysis (IGA) of the cured samples was carried out in circulating air at 650°F (343°C). The samples were cured under a nitrogen atmosphere at 250°C for 8 hrs and another 8 hrs at 350°C. The extended cure at 350°C was to assure that the systems would not contain any unreacted alkynyl groups (vide infra).

Since the AB-monomers contain both the diene, namely, benzocyclobutene unit and the dienophile, i.e., the alkyne unit, on the same molecule, they possess the perfect stoichiometry for a Diels-Alder reaction. In an idealized situation, such a reaction will occur intermolecularly and constitute the major polymerization process. Since the alkynes can be polymerized by itself at sufficiently high temperature, it is, therefore, necessary to select judiciously the alkyne, whose homopolymerization will not interfere with the Diels-Alder reaction. Both the primary and secondary ethynyl groups were investigated in this study. The DSC (Figure 2) of the phthalimide containing a primary ethynyl group, 6, shows two reaction exotherms, 202°C and 269°C. The first exotherm relates to the homopolymerization of the ethynyl group prior to the in situ generation of the o-xylylene at 269°C. In the case of a secondary ethynyl function, there is a gap of at least 110°C between the reaction exotherm of benzocyclobutene and homopolymerization exotherm of the alkyne. Indeed, the DSC (Figure 3) of 5a, which bears a secondary ethynyl group together with a benzocyclobutene moiety exhibits a single reaction-exotherm maximum, with some small tailing. The reaction exotherm can be ascribed to encompassing the formation of o-xylylene and its subsequent Diels-Alder reaction with the ethynyl group.

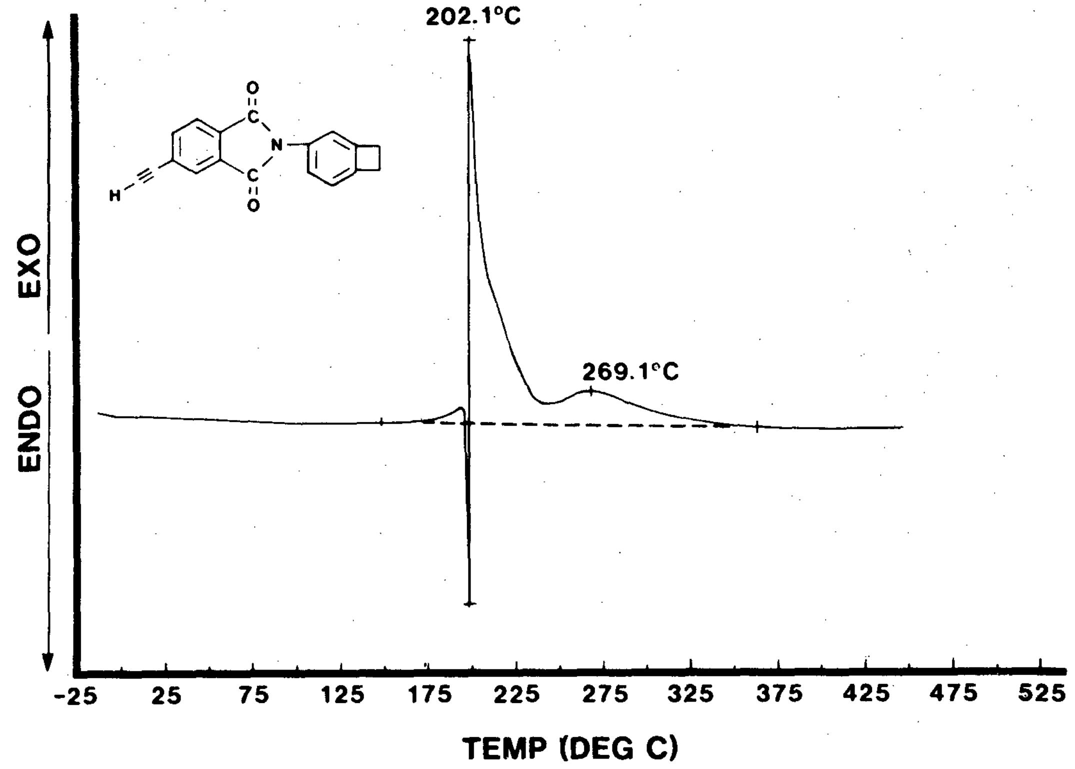


Figure 2. DSC thermogram of the AB-monomer, 6.

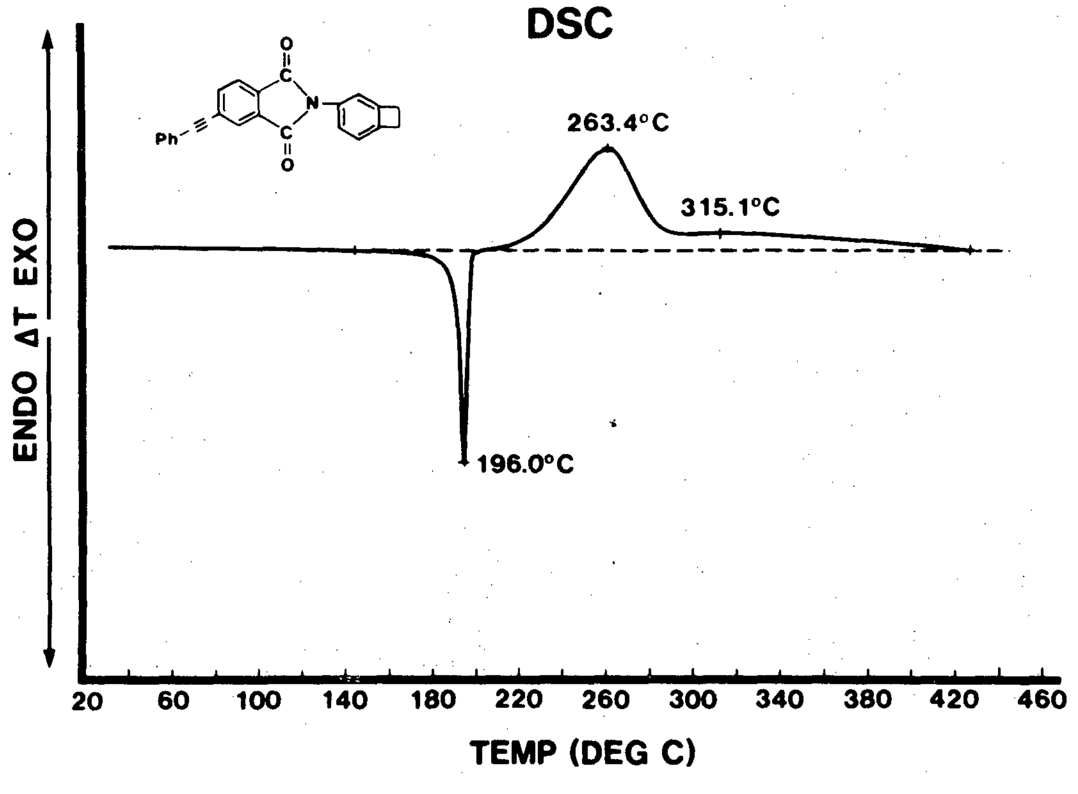
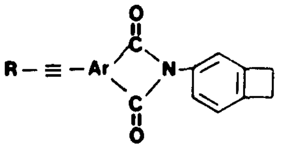
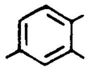
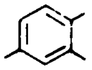
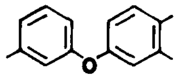
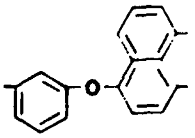


Figure 3. DSC thermogram of the AB-monomer, 5a.

However, when there is a phenoxy group connected between the phenylethynyl group and the imide fragment, the Diels-Alder reaction was greatly suppressed as evidenced by the appearance of a secondary exotherm attributable to the phenylethynyl homopolymerization. (See Figure 4 and Table 1.) The difference in the thermal behaviors of 6 and the other two AB-monomers, 9 and 12 can be rationalized on the basis of substituent effect. The alkynes are moderate dienophiles and quite sensitive to their terminal substitution. Terminal groups with strong electron withdrawing capacity greatly enhance the dienophilicity of the carbon-carbon triple bond, as exemplified by dimethyl acetylenedicarboxylate, one of the ubiquitous dienophiles in organic synthesis. Electron-donating groups, in the cases of 9 and 12, the phenoxy moiety, deactivate the reactivity of the alkynes toward dienes. Such rationale can also be applicable to the AABB system. (See Figure 1.)

Table 1: THERMAL PROPERTIES[a]



R	Ar	T_g	T_m	T_{poly}		T_g (CURE)[b]
				ONSET	MAX	
H		—	198	~170	202 270	—
Ph		—	196	209	263	278 (294)[c]
Ph		—	200	229 321	263 372	215
Ph		102	238	238 298	266 347	—

NOTE (a) ALL NUMERICAL VALUES ARE EXPRESSED IN °C. DSC WAS RUN AT HEATING RATE 20°C/MIN. (b) MEASUREMENTS WERE MADE ON SAMPLES PREVIOUSLY CURED UNDER N_2 ATMOSPHERE AT 250°C FOR 8 HRS AND THEN AT 350°C ANOTHER 8 HRS. (c) DETERMINED BY TMA

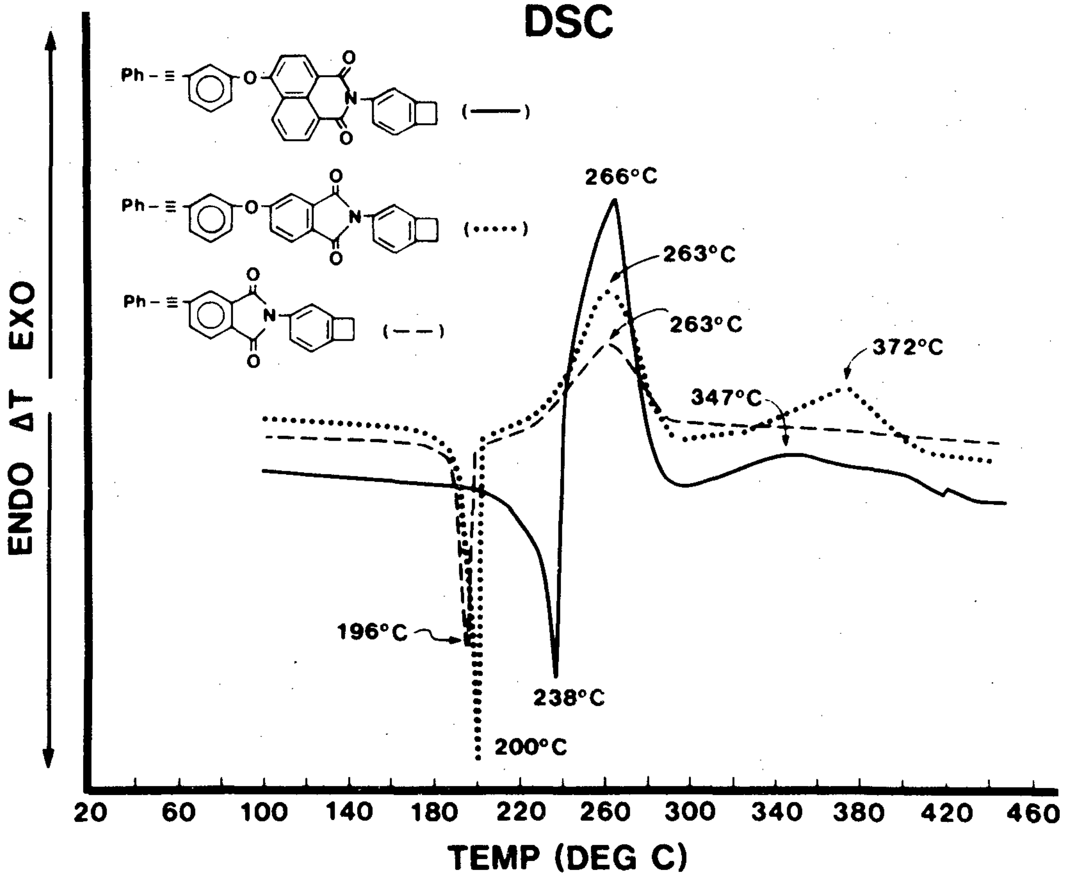


Figure 4: Comparative DSC thermogram of the AB-monomers 5a, 9, and 12.

The effect of incomplete Diels-Alder polymerization in the phenylethynyl/benzocyclobutene system is also reflected in the thermo-oxidative stabilities of the thermosets formed from the respective AB-monomers. (See Figure 5.) After 200 hrs at 650°F (343°C) in air, 5a suffers only 16-percent weight loss, whereas 9 and 12 lost 38 percent and 69 percent of their original weights, respectively. As mentioned earlier, 5a has the greatest extent of Diels-Alder polymerization (or lowest degree of phenylethynyl homopolymerization). The naphalimide system, 12, is the least thermoxidatively stable and its poor resistance to thermo-oxidative degradation may be attributed to the presence of the peri-hydrogen of the naphthalene nucleus, whose susceptibility to thermo-oxidative degradation has been shown by previous work from our laboratory[10]. Finally, with the exception of the thermosetting resins formed from 7, cured samples of 3a displays lower final glass transition temperature (Tg) than those of 4 and 10, which probably have higher cross-linking densities. We do not know, however, why cured 9 has the lowest final Tg (215°C). In all cases, the products generated were insoluble in the common organic solvents, indicating varying degrees of cross-linking reactions.

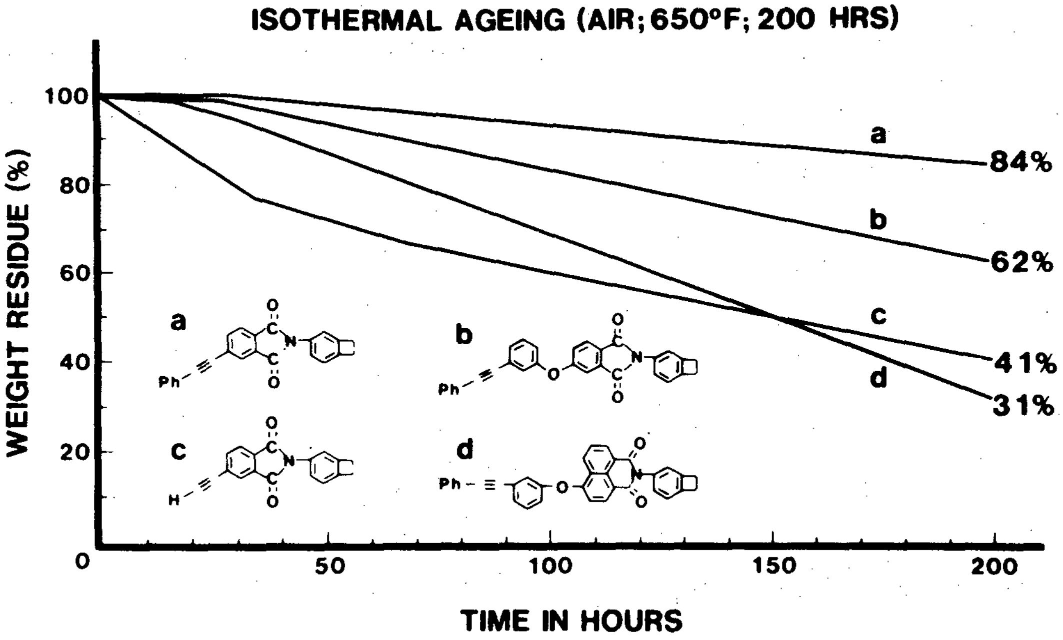


Figure 5: Isothermal aging study of the AB-monomers 5a, 6, 9 and 12.

SECTION III

CONCLUSION

On account of its capability to convert to a reactive diene under the mere influence of heat, benzocyclobutene has a wide latitude to combine with a variety of dienophiles. Such Diels-Alder polymerization can bring forth a range of thermoplastic and thermosetting polymers. In solid-state polymerization, the cycloaddition reaction is particularly advantageous because no void-forming volatile by-products are generated. In addition, the linear character (therefore, less brittle and tougher) of the resultant thermosets may be optimized by the right combinations of dienes/dienophiles to ensure the highest degree of Diels-Alder reaction. In the case of benzocyclobutene/alkyne combination, our study demonstrates that the final polymeric materials are heat-resistant, especially when the Diels-Alder cure pathway is maximized. This can only be accomplished with an activated alkyne group.

SECTION IV

EXPERIMENTAL

4-Bromophthalic anhydride was prepared from the alkaline bromination of phthalic anhydride, followed by cyclodehydration of the crude 4-bromophthalic anhydride in refluxing acetic acid[11]. Triethylamine was purified by distillation in the presence of barium oxide under N_2. Dry dimethyl sulfoxide (DMSO) was distilled from calcium hydride under reduced pressure. All other commercial reagents were used as received.

N-4-benzocyclobutenyl-4-bromophthahimide (4)

A mixture of 4-bromophthalic anhydride (12.4g, 54.6 mmoles) and 4-amino-benzocyclobutene (6.5g, 54.5 mmoles), freshly prepared from the catalytic hydrogenation of 4-nitro-benzocyclobutene, was gently refluxed in glacial acetic acid (120 ml) under nitrogen atmosphere for about 17 hrs. The resultant dark but homogeneous reaction mixture was allowed to cool to room temperature under N_2 and then poured into 750 ml of H_2O. Precipitation of gray solid immediately took place. Then, about 200 ml of CH_2Cl_2 was added to the mixture to deliver a two-phase solution. Subsequently, the CH_2Cl_2 layer was separated and the aqueous layer was extracted further with CH_2Cl_2 (2 x 50 ml). The combined CH_2Cl_2 extract was first concentrated to about 100 ml and then passed through a chromatography column (internal diameter, 2 cm., 110g silica gel, saturated with hexane). Elution of the column with hexane led to the isolations of the desired product, which crystallized out as beige microcystals upon rotary evaporation. The product was collected, washed with hexane and dried in vacu at 75°C overnight. Yield: 11.7g (65.4 percent, based on 4-aminobenzocyclobutene), m.p. = 167-168°C. Anal. Calc. for $C_{16}H_{10}BrNO_2$: C, 58.56; H, 3.07; N, 4.27; Br, 24.35. Found: C, 58.03; H, 3.20; N, 4.20; Br, 24.26. Mass spectroscopy: 327, 329 (31.24 percent, 35.51 percent, M^+). Proton NMR (δ values in ppm): 324 (singlet; alicyclic protons, 4 H; 7.17, 8.06 (complex; aromatic protons, 6 H). IR (KBr; in cm^{-1}) 2990 vw (aliphatic C-H stretches; 1775m, 1718 vs (imide linkage stretches).

N-4-Benzocyclobutenyl-4-phenylethynylphthalimide (5a)

A mixture of N-4-benzocyclobutenyl 4-bromophthalimide (3.75g 11.4 mmol), $Pd(OAc)_2$ (20 mg), PPh_3 (50 mg) were placed in a 3-necked 100-ml round-bottomed flask equipped with a condenser and a nitrogen adaptor. (All glasswares had been baked at 135°-140°C for 4 hrs, assembled while still hot, and allowed to cool to room temperature under a steady stream of N_2.) Then, 55 ml of triethylamine, freshly distilled from BaO was added to the reaction vessel and the orange, heterogeneous reaction mixture was heated, to reflux under N_2 for about 30 minutes. Then, the oil bath was removed and phenylacetylene (2.60g, 25.4 mmol) was added rapidly to the hot reaction mixture through the condenser. Immediately, quantitative amount of white solid (triethylammonium chloride) precipitated out, and greatly impeded the stirring of the reaction mixture magnetically. Hence, after the reaction vessel had been returned to the oil bath preheated to about 100°C, 5 ml of NEt_3 was added to facilitate stirring. The reaction mixture was gently refluxed for another 3 hrs and then at 40°C overnight. The light brown mixture, after cooling to room temperature, was poured into 300 ml H_2O. The resultant mixture was extracted with CH_2Cl_2 (100 ml, then 3 x 20 ml). The organic extract was subjected to rotary evaporation to afford 5.17g of crude brown solid, which was a mixture of the desired product and side products, PhC C$\equiv$C C$\equiv$Ph and PhC C=CH CHPh as suggested by mass spectroscopy. Column chromatographic purification of the crude product (internal diameter, 2 cm., 30g silica gel saturated with hexane, and eluting the CH_2Cl_2) led to crystallization of yellow-green microcrystals from the first fractions, after which were added with hexane and subjected to rotary evaporation at room temperature, repeatedly in that manner. Yield: 3.63g (91.2 percent), m.p. - 194-195°C. Anal. Calc. for $C_{24}H_{15}NO_2$: C, 82.50; H, 4.33; N, 4.01. Found: C, 81.78; H, 4.62; N, 4.06. Mass spectroscopy: m/e = 349 (M^+). HPLC purity 96 percent. Proton NMR (δ values in ppm): 3.21 (singlet; alicyclic protons, 4 H); 7.31, 8.03 (complex; aromatic protons, 11 H) (Figure 6). IR (KBr, in cm^{-1}); 2954 w, 2929 vw, 2904 w (alicyclic C-H stretches); 2208 w (-C≡C- stretch); 1769m, 1695 vs (imide linkage stretch) (Figure 7).

N-4-Benzocyclobutenyl-4-trimethylsilylethynylphthalimide, (5b)

N-4-benzocyclobutenyl 4-bromophthalimide (4.00g, 12.2 mmol), palladium acetate (24 mg), triphenylphosphine (48 mg) and 60 ml of dry NEt_3 were placed in a 100-ml 3-necked round-bottomed flask equipped with a thermometer, reflux condenser and N_2-adaptor. The resultant reaction mixture was refluxed under N_2 for about 15 minutes. Then, it was allowed to cool slowly to room temperature under N_2. Trimethylsilylacetylene (2.50g, 25.4 mmol) was introduced into the reaction mixture via the reflux condenser. Immediately, a quantitative amount of white solids precipitated. The reaction mixture was then heated at 100°C for about 3 hr and stirred at room temperature overnight under N_2. The brown heterogeneous mixture was poured into about 300 ml of H_2O and extracted with CH_2Cl_2 (2 x 100 ml + 2 x 50 ml). The CH_2Cl_2 extract was then washed with 200 ml H_2O and dried over $MgSO_4$. Upon removal of the solvent, a mixture of white and brown solids was obtained. The mixture was washed with 250 ml of H_2O and air-dried for an hour. It was then dissolved in 50 ml of CH_2Cl_2 and the resultant solution was passed through a short column containing 25g of silica gel saturated with hexane. Elution with 1:1 CH_2Cl_2/hexane led to the isolation of microcrystalline tan solid from the first fraction. Yield: 4.0g (95 percent) mp = 192-193°C. Anal. Calc. for $C_{21}H_{19}NO_2Si$: C, 73.01; H, 5.54; N, 4.05. Found: C, 72.95; H, 5.45; N, 4.01. Mass Spectroscopy: 345 (M^+, 100 percent). Proton NMR ($CDCl_3$):

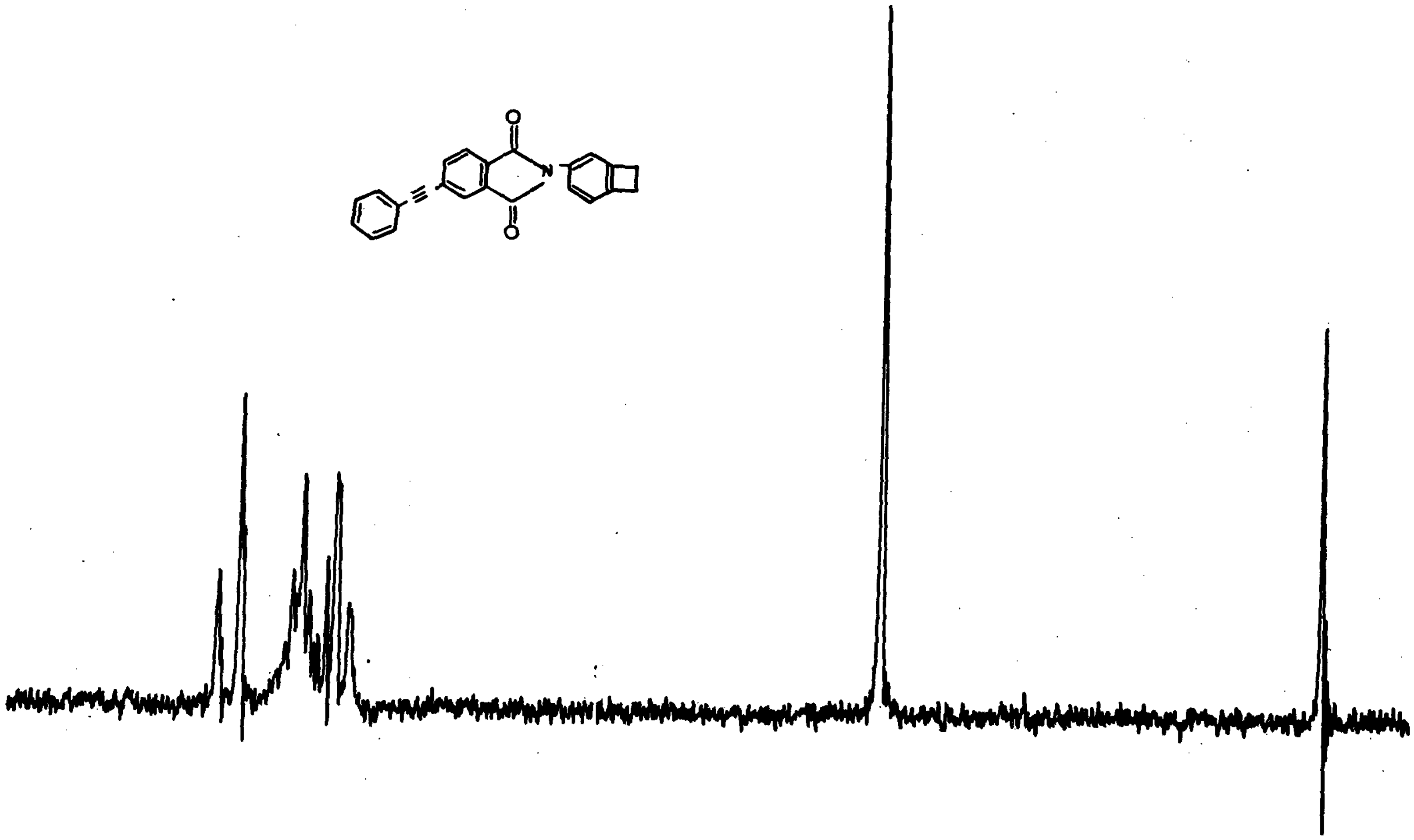


Figure 6. ^1H NMR Spectra of AB-monomer 5a.

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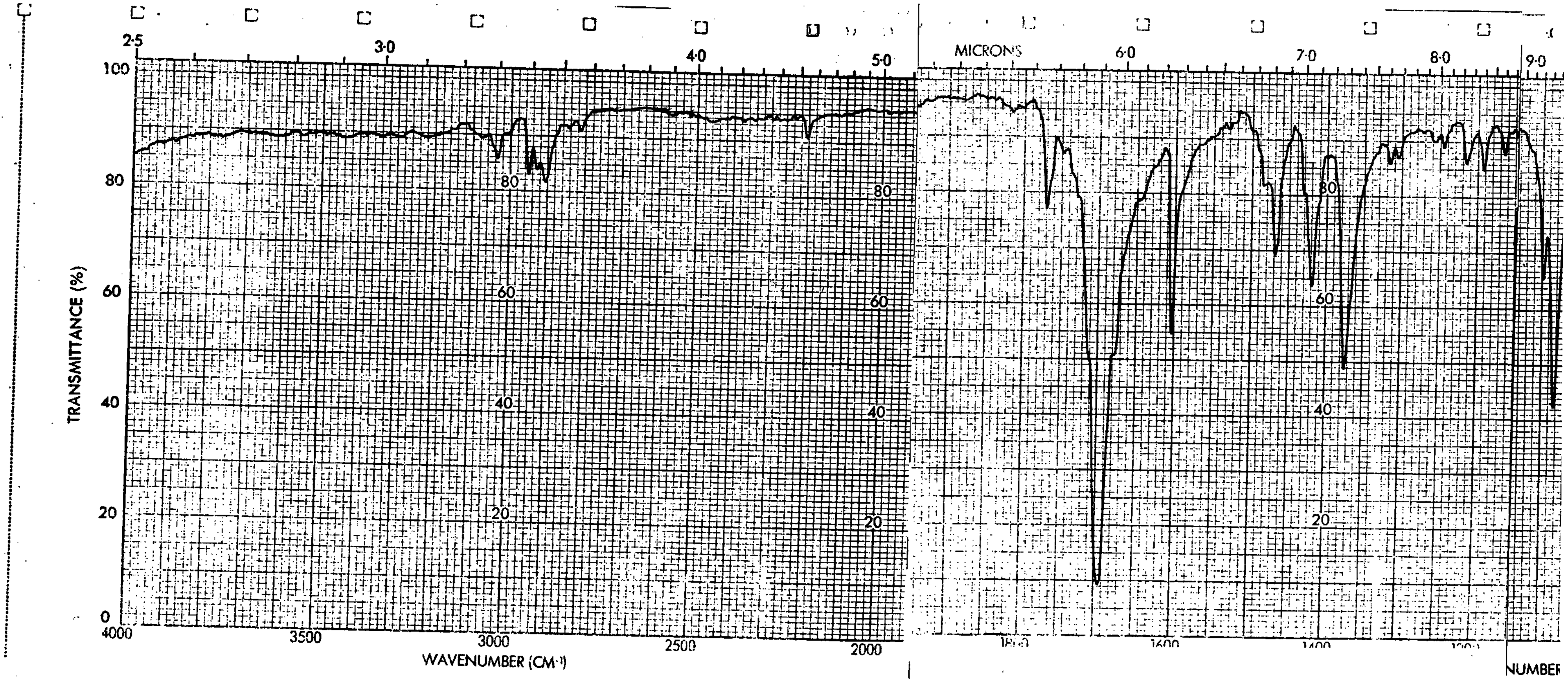

Figure 7. Infrared Spectra of AB-monomer 5a.

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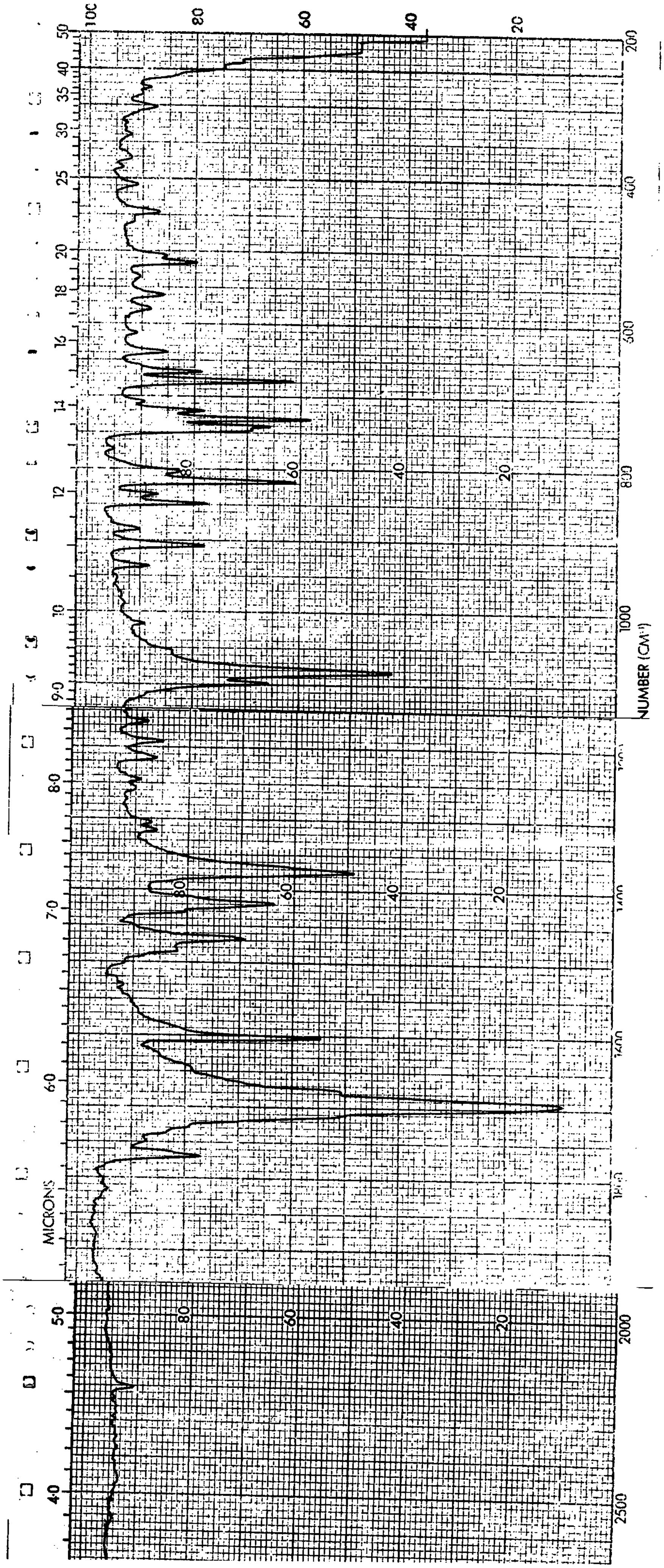

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NUMBER (CM⁻¹)

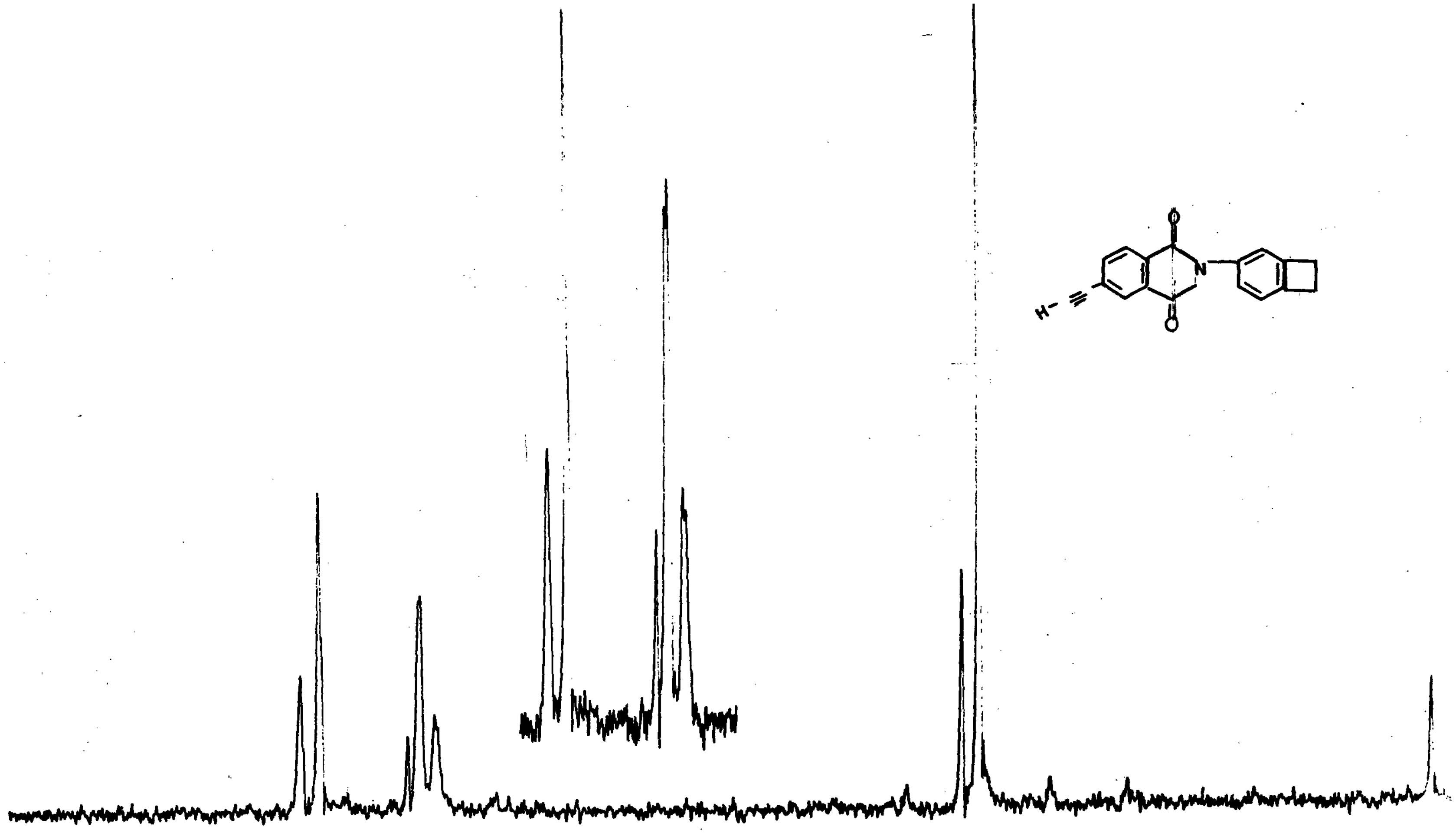


Figure 8. ^1H NMR Spectra of AB-monomer 6

1of2

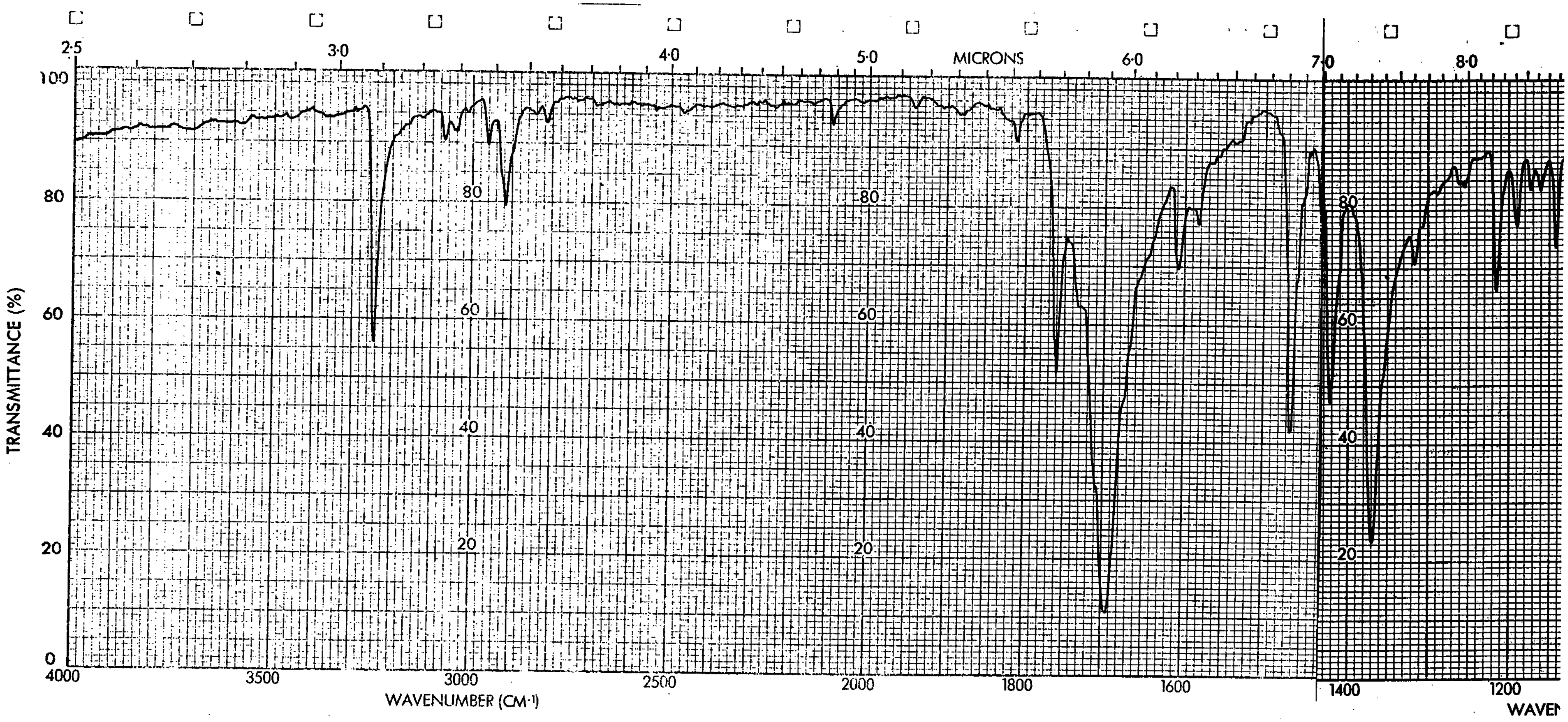
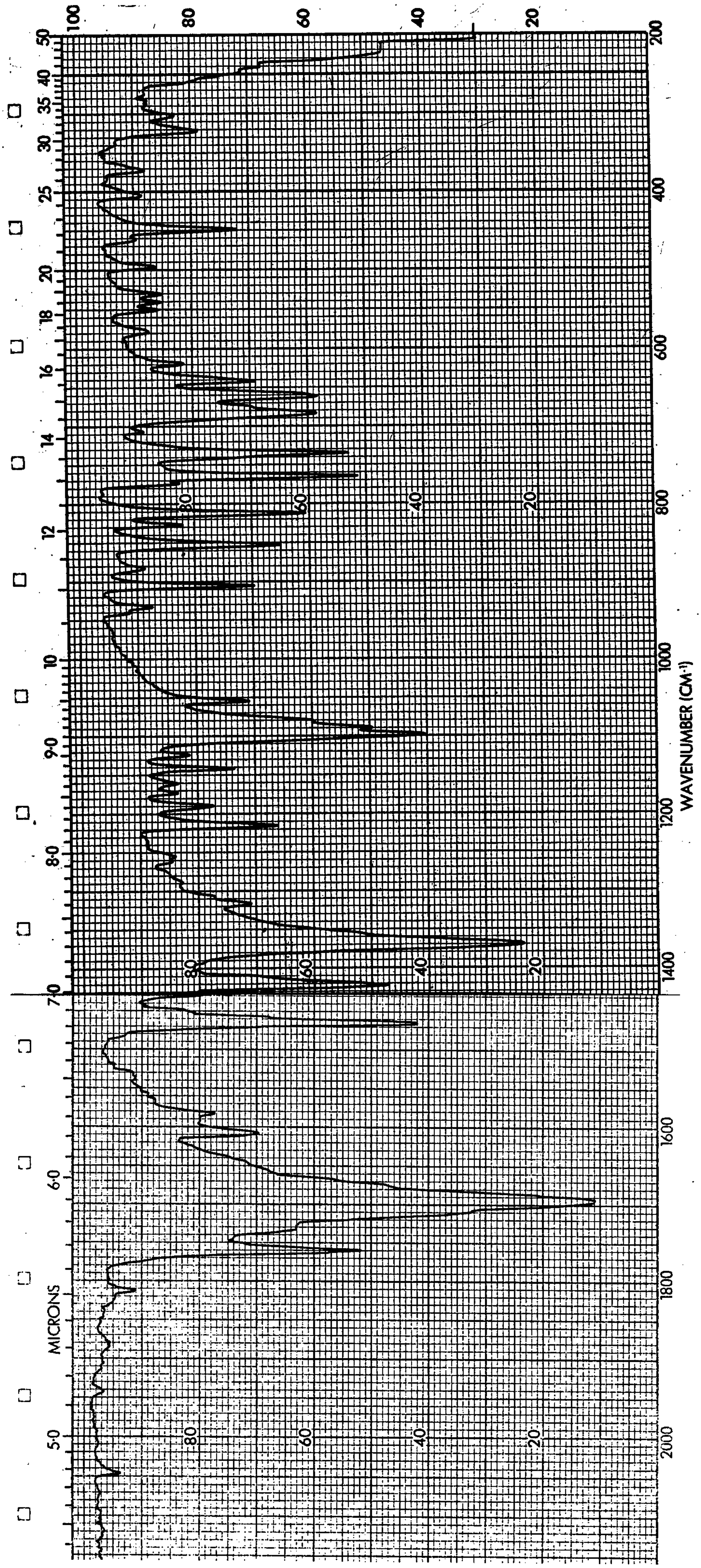


Figure 9. Infrared Spectra of AB-monomer 6.

2of2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7·0
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WAVENUMBER (CM-1)
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400
600
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1000
1200
1400
1600
1800
2000

3-Bromophenyl trimethylsilyl ether (14)

We placed 3-Bromophenyl (17.3g, 0.100 mol) and 9 ml of pyridine together with 100 ml of toluene in a 3-necked 250-ml round-bottomed flask equipped with a reflux condenser, an additional funnel, and thermometer/adaptor. Chlorotrimethylsilane (12.8gl, 15 ml, 0.12 mol) was added dropwise to the vigorously stirred solution. The resultant white reaction mixture was subsequently refluxed for 4 hrs and then stirred at room temperature overnight. The white precipitate was removed by filtration and the colorless filtrate was subjected to rotary evaporation to remove the solvent. The residual liquid was purified by simple distillation. The pure product was collected at 232-233°C. Yield: 23.0g (93 percent). Anal. Calc. for $C_9H_{13}BrOS$; C, 44.08; H, 5.34; Br, 32.59. Found: C, 43.98; H, 5.36; Br, 32.35. Mass spectroscopy: 244-246 (77 percent, 78 percent, M^+). Proton NMR (δ in ppm, $CDCl_3$); 0.27 (singlet, Me_3Si-_; 6.66-7.32 (complex, aromatic).

N-4-Benzocyclobutenyl 4-nitro-naphthalimide (10)

A mixture of 4-nitronaphthalic anhydride (2.07g, 8.51 mmol) and 4-aminobenzycyclobutene (1.10g, 9.23 mmol) was stirred in acetic acid (100 ml)/toluene (80 ml) at room temperature for about 1/2 hr and then heated to reflux under N_2. The reaction mixture turned dark and homogeneous upon reflux. The water of imidation was removed azeotropically via a Dean-Stark trap. After about 17 hrs of reflux, the reaction mixture was cooled to room temperature and poured into about 600 ml of 20-percent aqueous NaCl solution. After extraction with ethyl acetate until the aqueous layer was almost colorless and clear, the organic extract was washed with saturated NaCl solution (2 x 500 ml) and then dried over $MgSO_4$. Upon complete removal of the solvent by rotary evaporation, the extract yielded a brown solid as the crude product, which was dissolved completely in CH_2Cl_2 and filtered through a bed of silica gel (10g), washing with CH_2Cl_2 until the filtrate was colorless. Complete evaporation of the filtrate led to the isolation of a yellow powder. Yield: 2.60g (88.7 percent). Anal. Calc. for $C_{20}H_{12}N_2O_4$; C, 69.76; H, 3.51, N, 81.38. Found: C, 69.66; H, 3.51; N, 81.24. Proton NMR ($CDCl_3$): 3.30 (singlet, alicyclic protons); 7.05-9.04 (complex, aromatic protons). IR(KBr); 2940w (alicyclic C-H stretch); 1720 ms, 1675 vs (carbonyl stretches of imide group); 1530s, 1350s (asymmetric and symmetric stretches of nitro group).

N-4-Benzocyclobutenyl-4-nitrophthalimide (7)

A mixture of 4-nitrophthalic anhydride (3.46g, 17.9 mmol) and 4-aminobenzycyclobutene (2.20g, 18.5 mmol) was refluxed in acetic acid under N_2 for about 17 hours. The dark reaction mixture was then allowed to cool to room temperature and poured into 500 ml of H_2O, followed by extraction with CH_2Cl_2 ((75 ml + 3 x 50 ml). The dark extract was then washed with 300 ml of H_2O and then dried over $MgSO_4$. Complete removal of CH_2Cl_2 from the extract by rotary evaporator afforded a dark oil, which was purified by column chromatography (150g silica gel); using 1:1 petroleum ether/CH_2Cl_2 as eluent). Pure product was isolated from the first fraction as yellow solid. Yield: 3.21g (65 percent). Anal. Calc. for $C_{16}H_{10}N_2O_4$; C, 65.30; H, 3.42; N, 9.52. Found C, 65.21; H, 3.39; N, 9.58. Mass spectroscopy: 294 (M^+, 100 percent). Proton NMR ($CDCl_3$): 3.24 (singlet, alicyclic protons); 7.00-7.23, 8.06-8.72 (complex, aromatic protons). IR(KBr): 2900w, 2770m, 2650m (alicyclic C-H stretches); 1720, 1775 (symmetric and asymmetric stretches of imide group); 1350, 1540 (symmetric and asymmetric stretches of nitro group).

Preparation of AB monomer (12)

We placed 3-hydroxytolane (0.30g, 1.54 mmol), 1.55 ml of standardized (1N) methanolic KOH solution and 65 ml of toluene in a 100-ml 3-necked round-bottomed flask. The resultant dark-red solution was subjected to simple distillation under N_2. About 55 ml of distillate was collected. After the temperature of the mixture was allowed to cool to about 50°C, dry DMSO (60 ml) was introduced to dissolve completely the dark brown solid that formed. The resultant homogeneous, dark solution was distilled again until the head temperature was about 115°C (pot temperature: 144-150°C), About additional 5 ml of toluene was collected. After the dark phenolate solution was allowed to cool to about 35°C in an oil bath, N-4-benzocyclobutenyl-4-nitro-naphthalic imide (0.53g, 1.54 mmol) was added neat under N_2. The reaction mixture was stirred at 35-40°C for about 1-1/2 hr and then allowed to cool to room temperature. It was poured into a separatory funnel containing 300 ml of H_2O, and extracted with CH_2Cl_2 (50 ml, then 3 x 25 ml). The combined extract was then dried over $MgSo_4$. The volume of dried extract was reduced to about 1/3 its original volume and then passed through a short column containing about 20g silica gel, saturated with petroleum ether. The column was then eluted with 1:1 petroleum ether/CH_2Cl_2. The collected yellow solution was concentrated and chilled overnight to afford yellow microcrystals. Yield: 0.55g (77 percent), m.p. 235-236°C. Anal. Calc. for $C_{34}H_{21}NO_3$: C, 82.97; C, 83.08; H, 4.31; N, 2.85. Found: C, 82.97; H, 4.25; N, 2.90. Mass spectroscopy: 491 (M^+, 75.7 percent). Proton NMR ($CDCl_3$): 3.21 (singlet, alicyclic protons); 6.88-7.89, 8.41-8.72 (complex, aromatic protons) (Figure 10), IR(KBr): 2705m (alicyclic CH Stretch); 1710ms, 1670vs (symmetric and asymmetric stretches of imide group); 1240vs (Ar-O-Ar stretch) (Figure 11).

Preparation of AB-monomer (9)

We placed 3-hydroxytolane (0.69g, 3.55 mmol), 3.6ml of standardized methanolic KOH solution (3.60 ml, 3.60 mmol) and 75 ml of toluene in a 100-ml

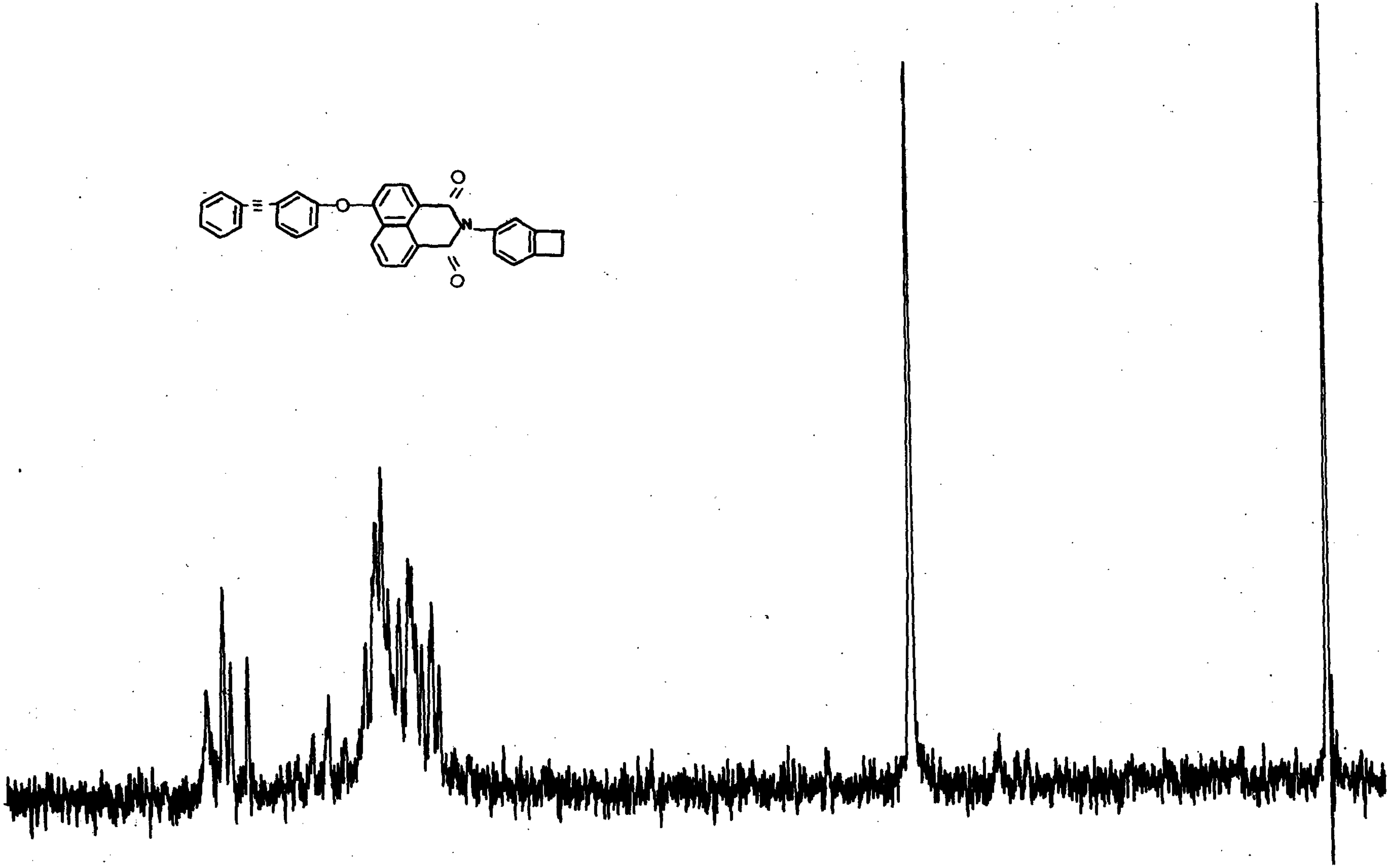

Figure 10. ^1H NMR Spectra of AB-monomer 12.

1of2

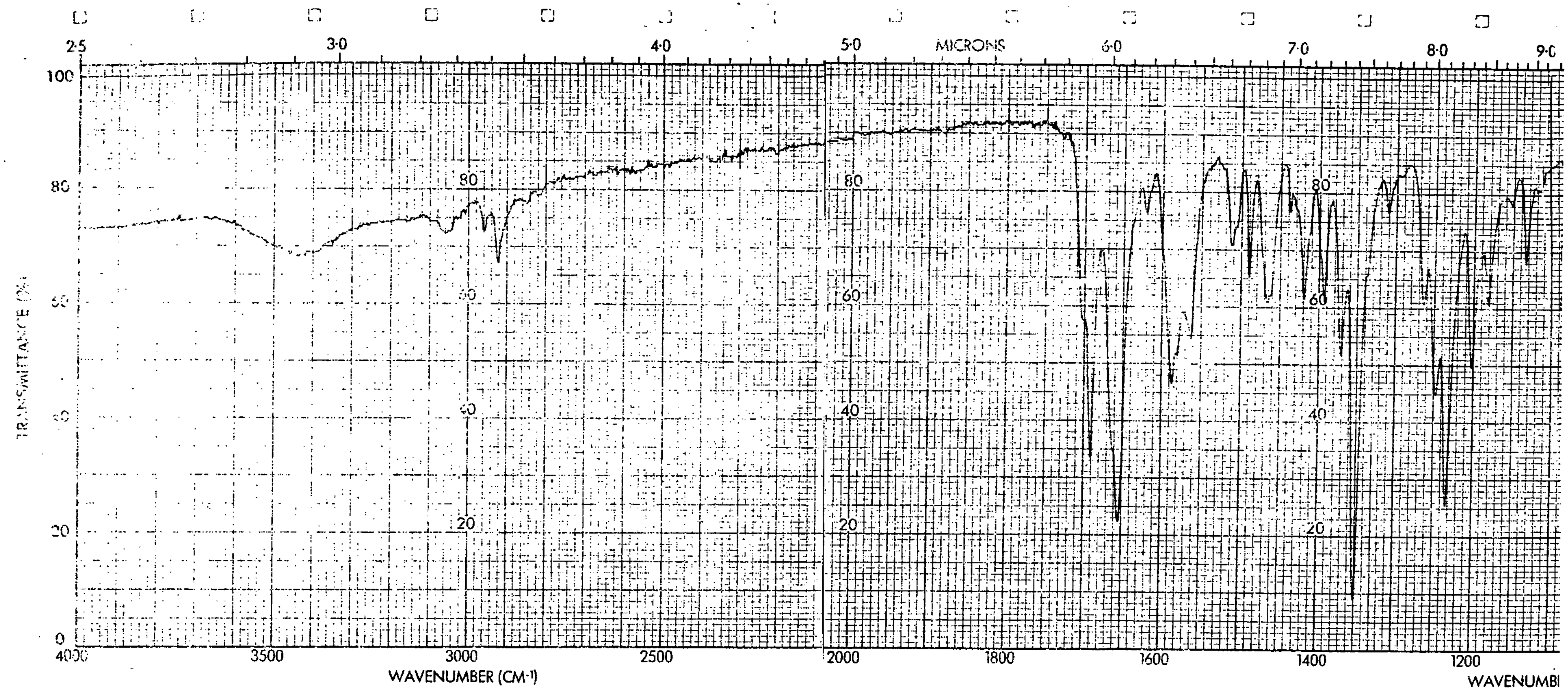

Figure 11. Infrared Spectra of AB-monomer 12.

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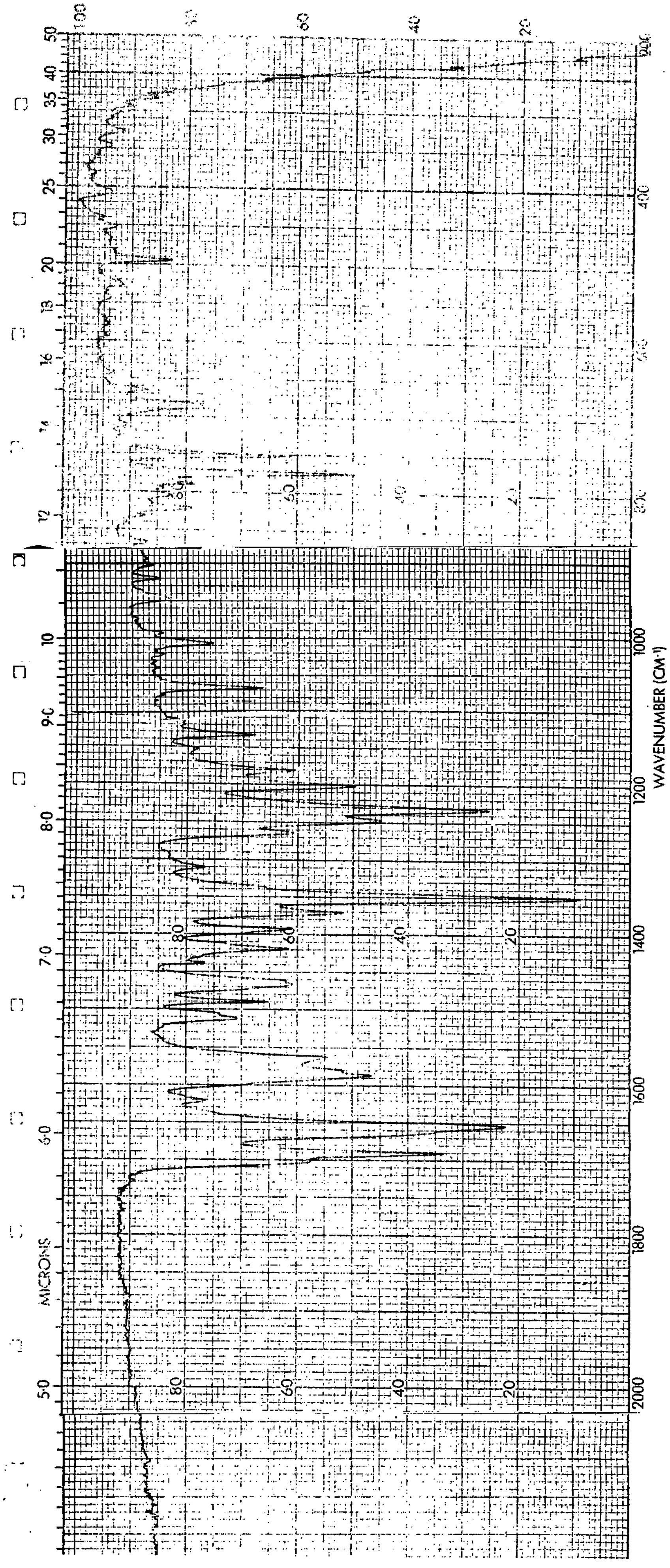
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WAVENUMBER (CM⁻¹)
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20

dark brown crude produce (about 5.0g). Proton NMR ($CDCl_3$); 5.18 (singlet, -OH), 6.71-7.67 (complex, aromatic H). The hydroxyl proton is readily exchanging with denterium of D_2O. IR(KBr): resultant reaction mixture was stirred under N_2 at 30-35°C for another 2-1/2 hours. Then, the reaction mixture was poured into a separatory funnel containing about 300 ml of H_2O and extracted with ethyl acetate (100 ml, 3 x 50 ml). The organic extract was then washed with saturated NaCl solution (2 x 150 ml) and dried over $MgSO_4$. The volume of the dried extract was concentrated on a rotary evaporator to about 10 ml and passed through a chromatographic column containing about 100g of silica gel saturated with petroleum ether. Elution was carried out with 100 ml of petroleum ether, followed by 1:2 CH_2Cl_2/petroleum ether. Four bands were developed in the column. The desired product which was contained in the first band, was isolated as light yellow microcrystals. Yield: 0.45g (30 percent). Anal. Calc. for $C_{24}H_{14}NO_3$: C, 81.62; H, 4.34; N, 3.17. Found: C, 81.05; H, 4.31; N, 3.09. Mass spectroscopy: 441 (M^+, 100 percent). Proton NMR ($CDCl_3$); 3.20 (singlet, alicyclic protons), 7.00-7.93 (complex, aromatic protons) (Figure 12). IR(KBr) 2700m (alicyclic C-H stretches); 1706m, 1778vs (symmetric and asymmetric stretches of imide group); 1238 ms (Ar-O-Ar stretch) (Figure 13).

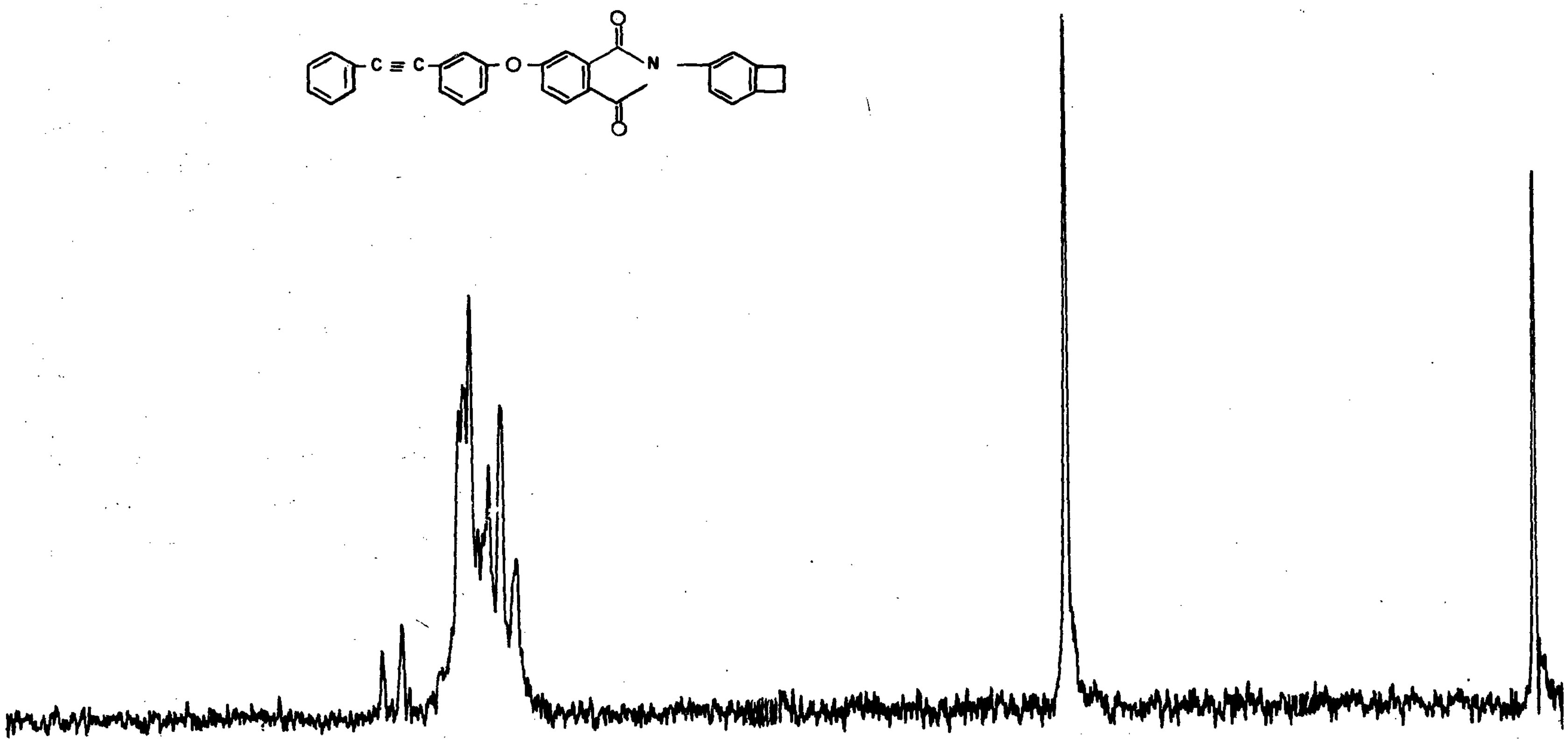

Figure 12. ^1H NMR Spectra of AB-monomer 9.

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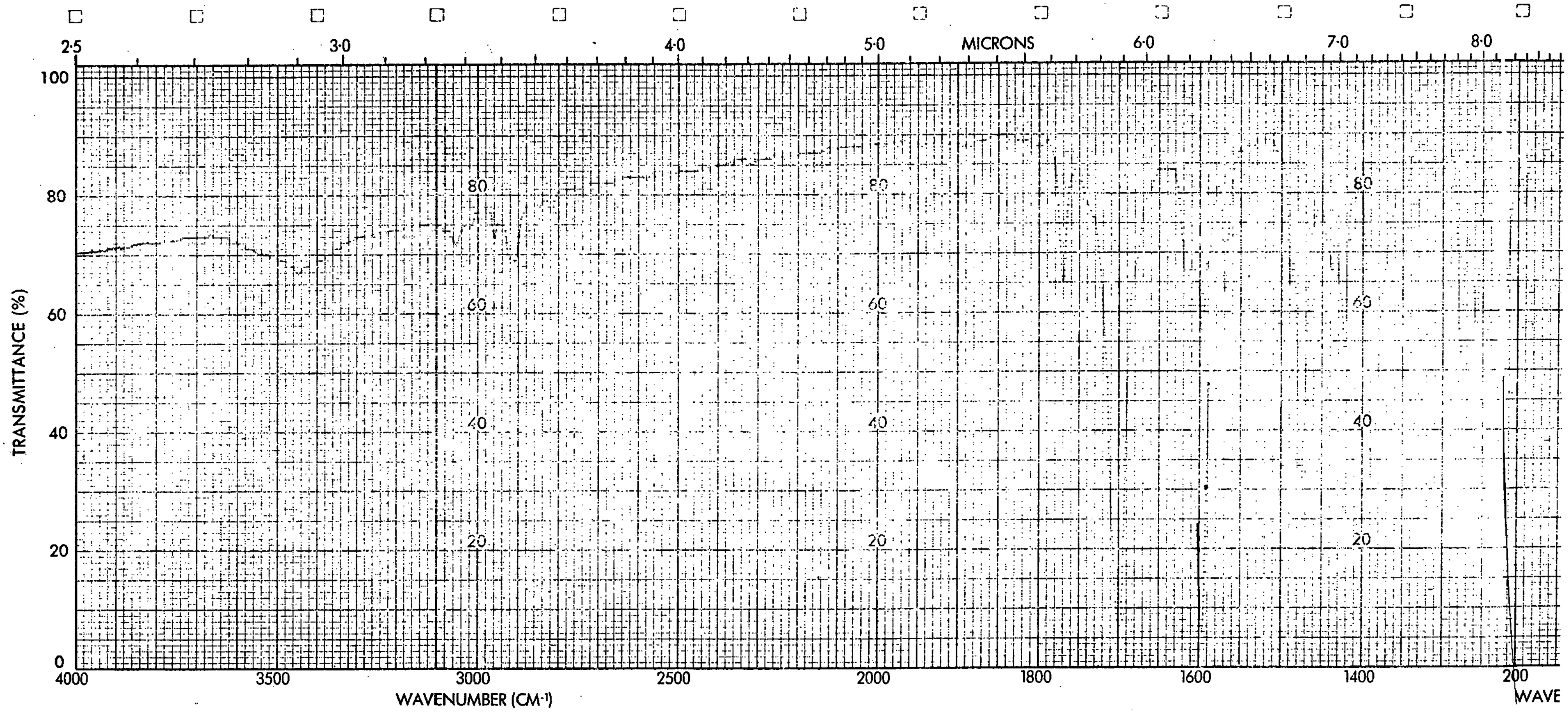

Figure 13. Infrared Spectra of AB-monomer 9.

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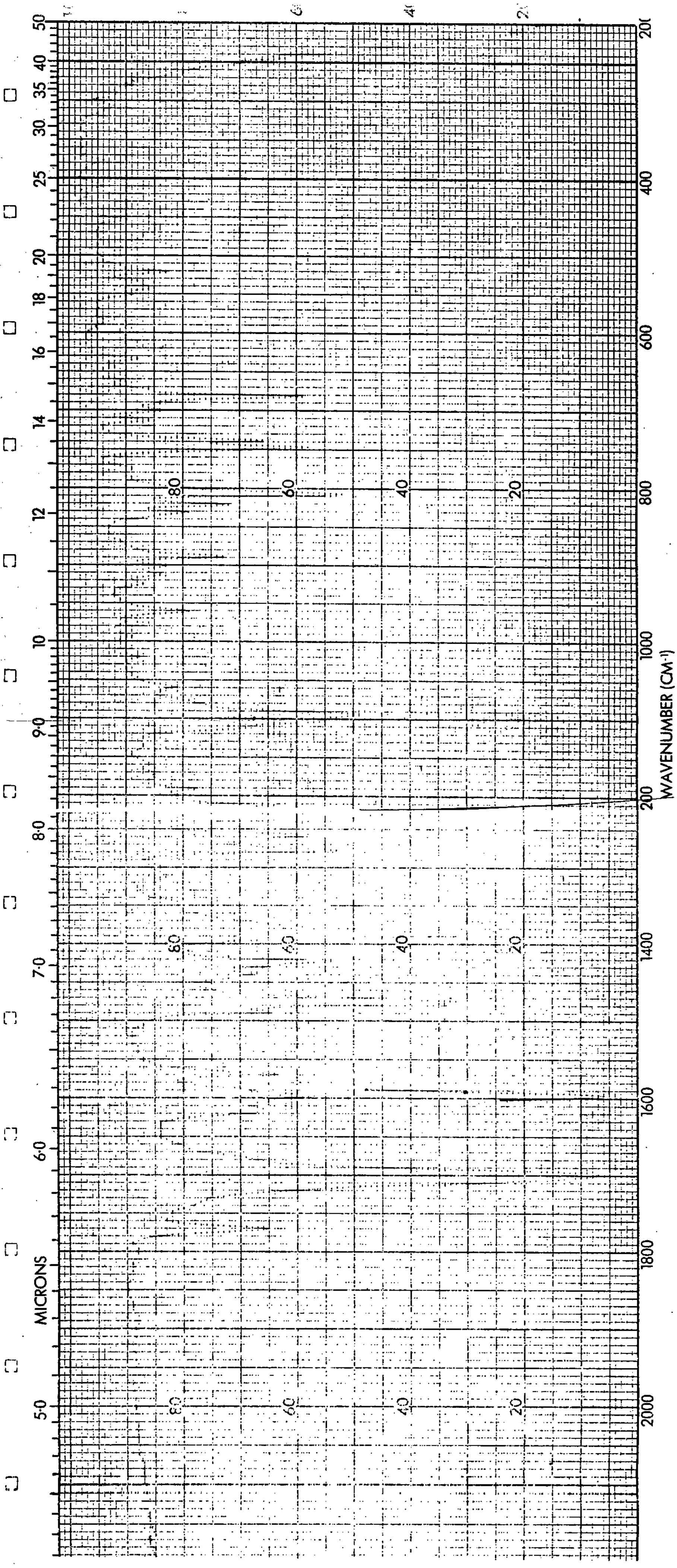
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