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journal or publication title	Journal of Photopolymer Science and Technology
volume	29
number	3
page range	495-500
year	2016
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URL	http://hdl.handle.net/10112/11221

doi: 10.2494/photopolymer.29.495

Communication

Journal of Photopolymer Science and Technology
Volume 29, Number 3 (2016) 495 – 500 ©2016SPST

Synthesis and Resist Properties of Calixarene Polymers with Pendant Haloalkyl Groups

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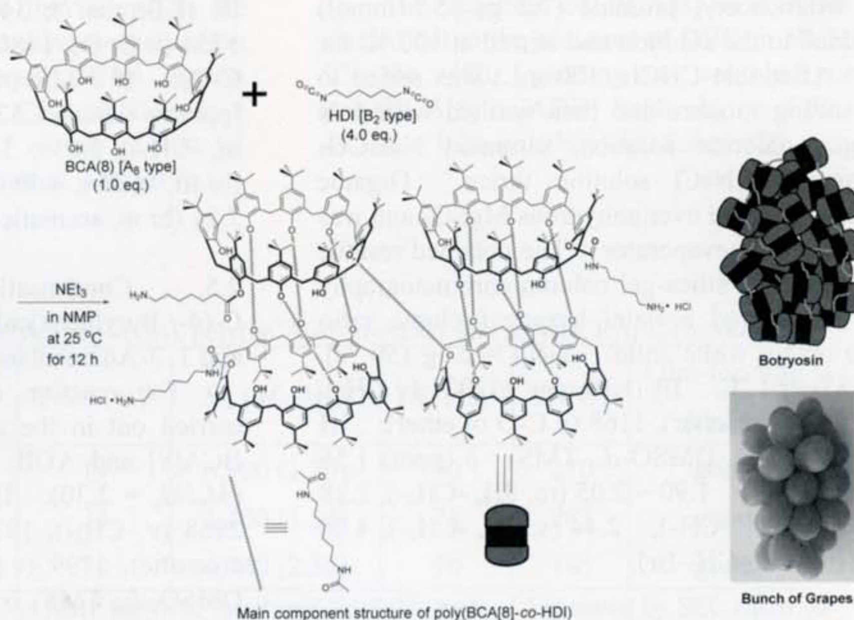
Keywords: calixarene, botryosin, electron beam, extreme ultraviolet, resist

1. Introduction

Calixarenes (CA's) are cyclic oligomers with pendant many hydroxyl groups and are easily synthesized by the condensation reaction of phenols and aldehydes in satisfactory yields under dynamic covalent chemistry system [1]. The synthesis and property of various calixarenes such as *p*-*t*-butylcalix[8]arene (BCA[8]), *p*-methylcalix[6]arene (BCA[6]), *c*-methylcalix[4]resorcinarene (CRA[4]), and *c*-(4-hydorxybenz)calix[4]resorcinarene (CRA-OH[4]) have been reported [2,3]. Their derivatives with pendant functional groups can be also synthesized easily.

Furthermore, polymers bearing CA moieties in the main or side chains (CA-polymers) have also been synthesized and they have potential applications as chemical sensors, selective membranes, and catalysts, as well as in microelectronic devices [4-6]. Very recently, we considered the synthesis of three dimensional cross-linking materials including calixarene moieties and expected that higher selectivity with some metal ions might show in the comparison of CA's derivatives. Indeed, when we examined the polyaddition reaction of BCA[8] and 1,6-hexanediisocyanate (HDI) in the presence of NEt_3 in NMP at 25 °C for 12 h, no gel compound could be obtained and only soluble copolymer poly(BCA[8]-*co*-HDI) was obtained in quantitative yield. Analysis by ^{1}H NMR, IR, MALDI-TOF mass spectroscopy, and AFM indicated that poly(BCA[8]-*co*-HDI) consists of nanoscale-gel-shaped structures that contain fixed holes and cavities resembling a bunch of grapes



Scheme 1. Synthesis of botryosin-type polymer by the polyaddition of BCA[8] and HDI.

Received April 1, 2016
Accepted May 11, 2016

(Scheme 1). We designated this class of polymers as botryosin, after the Greek word botrys, meaning a bunch of grapes [7].

In this time, we examined the condensation reaction of BCA[8] and adamantan derivative (AD) containing carboxylic acid groups, anticipating that soluble polymers have botryosin-like structure and ester groups in the main chain can be decomposed, to offer higher resolution resist pattern. The synthesis and resist properties of the polymers by the polycondensation of BCA[8] as a A_8 type monomer with AD as a B_2 type monomer.

2. Experimental

2.1. *p-t*-Butylcalix[8]arene (BCA[8]), *p-t*-Butylcalix[4]arene (BCA[4]), and C-(4-*t*-butylbenz)calix[4]resorcinarene (BCRA[4])

BCA[8] and BCA[4] were commercial available used. C-(4-*t*-butylbenz)calix[4]resorcinarene (BCRA[4]) was synthesized by the condensation reaction of resorcinnol and 4-*t*-butylbenz aldehyde using HCl as a catalyst in ethanol at 80 °C for 20 min in 51% yield.

2.2. Synthesis of 1,3-Adamantane Dibromoacetate (ADB)

Typical procedure: A solution of 1,3-adamantanediol (2.00 g, 11.9 mmol) 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (5.4 g, 35.7 mmol) in NMP (10 mL) was prepared at 0 °C. Then, bromoacetyl bromide (7.2 g, 35.7 mmol) was added to the solution and stirred at 100 °C for 24 h. After that $CHCl_3$ (100 mL) was added to the resulting mixture and then washed with 1 N hydrogen chloride solution, saturated $NaHCO_3$ solution, and NaCl solution thrice. Organic solution was dried over anhydrous $MgSO_4$ and was concentrated by evaporator. The obtained residue was purified by silica-gel column chromatography eluted with ethyl acetate/ hexane (volume ratio 1/1) to obtain white solid. Yield = 2.4g (50 %). Mp = 57 ~ 61 °C. IR (KBr, cm^{-1}): 2921 (ν CH_2), 1745 (ν C=O of ester), 1168 (ν C-O of ether). ^{1}H NMR (400MHz, DMSO-d_6, TMS) : δ (ppm) 1.56 (s , 2H, -CH_2-) 1.90 ~ 2.05 (m, 8H, -CH_2-), 2.28 ~ 2.35 (br, 2H, >CH-), 2.44 (s, 2H, -CH_2-), 4.26 ~ 4.30 (m, 4H, -CH_2-Br).

2.3. Condensation Polymerization of *t*-Butylcalix[8]arene (BCA[8]) and 1, 3-Adamantane Dibromoacetate (ADB)

Typical procedure: A solution of BCA[8] (1.95 g, 1.5 mmol), tetrabutylammonium bromide (TBAB) (1.51 g, 0.5 mmol), and NaH (0.288 g, 12 mmol) in NMP (30 mL) was stirred at 80 °C for 3 h. Then, ADB (2.45 g, 6.0 mmol) was added, and the reaction mixture was stirred at 80 °C for 48 h. The resulting mixture was poured into a large amount of 1 N hydrogen chloride solution to precipitate a solid, which was collected by filtration on a membrane filter (Millipore LAWPO 4700 pore size 0.45 μm). The obtained solid was purified by silica-gel column chromatography eluted with $CHCl_3$. The resulting residue was soluble in $CHCl_3$ and poured into large amount of methanol to precipitate the solid. The molecular weights were estimated by SEC and their structure was confirmed by ^{1}H NMR spectroscopy. Yield = 0.68 g (19 %). M_n = 6,900 (M_w/M_n = 1.20). IR (KBr, cm^{-1}): 3464 (ν -OH), 2954 (ν -CH_2-), 1735 (ν C-O-C), 1481 (ν C=C of aromatic), 1187 (ν C-O of aromatic). ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ (ppm) = 0.66 ~ 1.34 (br m, -CH_3), 1.34 ~ 1.65 (br m, -CH_2-), 1.82 ~ 2.10 (br m, -CH_2-), 2.10 ~ 2.35 (br m, >CH-), 3.65 ~ 4.81 (br m, -O-CH_2-), 6.33 ~ 7.56 (br m, aromatic H).

2.4. Condensation Polymerization of *p-t*-Butylcalix[4]arene (BCA[4]) and 1, 3-Adamantane dibromoacetate (ADB)

The reaction of BCA[8] and ADB was carried out in the same way for the reaction of BCA[8] and ADB. Yield =24%. M_n = 1,400 (M_w/M_n = 1.34). IR (KBr, cm^{-1}): 3472 (ν -OH), 2953 (ν -CH_2-), 1754 (ν C=O), 1480 (ν C=C of aromatic), 1183 (ν C-O). ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ (ppm) = 0.81 ~ 1.32 (br m, -CH_3), 1.71 ~ 1.96 (br m, -CH_2-), 3.01 ~ 3.37 (br m, -CH_2-), 4.09 ~ 4.48 (br m, >CH-), 4.49 ~ 5.17 (br m, -O-CH_2-), 6.30 ~ 7.21 (br m, aromatic H).

2.5. Condensation Polymerization of C-(4-*t*-Butylbenz)calix[4]resorcinarene (BCRA[4]) and 1, 3-Adamantane Dibromoacetate (ADB)

The reaction of BCRA[4] and ADB was carried out in the same way for the reaction of BCA[8] and ADB. Yield = 78%. M_n = 4,740 (M_w/M_n = 2.30). IR (KBr, cm^{-1}): 3450 (ν -OH), 2958 (ν -CH_2-), 1734 (ν C=O), 1496 (ν C=C of aromatic), 1199 (ν C-O). ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ (ppm) = 0.80 ~ 1.41 (br m, -CH_3), 1.38 ~ 2.64 (br m, -CH_2-), 3.80 ~ 4.88 (br m, -CH_2-b and >CH-), 5.95 ~ 7.61 (br m, aromatic H).

2.6. Thickness Loss Property on the Silicon Wafer after Soaking in 2.38 wt% Tetramethylammonium Hydroxide (TMAH) aq. Solution

The solutions of poly(BCA[8]-*co*-ADB), poly(BCA[4]-*co*-ADB), and poly(BCRA[4]-*co*-ADB) in propylene glycol monomethyl ether acetate (PGMEA) were spin-coated on the silicon wafer to prepare corresponding thin films with about 50 nm thickness. The value of thickness of the thin films was determined by ellipsometry before and after soaking in TMAH aq. for 30 sec.

2.7. Resist Sensitivity

The resist solutions were filtered through a 0.20 μm PTFE syringe filter prior to spin-coating on silicon wafers which were primed with hexamethyldisilazane (HMDS). Spin-coating was performed at 3000 rpm for 30 s to form thin films on the silicon wafers. Then these spin-coated films were prebaked at 150 °C for 60s. The film thickness was adjusted to 100 nm. The resulting films were exposed to EUV lithography (energetic EQ-10M) [8]. The area of exposure was approximately 1 × 1 cm^2. After the exposure, they were developed by dipping in THF at 23 °C for 30 s and then rinsed in deionized water before drying. The resist film thickness was measured with an ET200 surface profiler to obtain sensitivity curves.

2.8. Etching Durability

The etching rates of the thin films on the silicon wafers were determined using a reactive ion etching (RIE) plasma process. The plasma conditions were a 15 SCCM CF_4 gas flow, a 5 sccm Ar gas flow, and an RF power of 100 W. The pressure in the process chamber was 1.0 Pa.

2.9. EB Patterning Property

The mixture of polymer and triphenylsulfonium perfluoro-l-butanesulfonate (TPS-PFBS) as a photo-acid generator (PAG) was dissolved in PGMEA, which feeds weight-% ratio was as follow.; polymer / TPS-PFBS / trioctylamine = 100 / 10 / 1.25. The spin-coating thin films on the silicon wafers were soft baked (SB) at 170 °C under N_2 gas flow. The films were exposed to a 75 kV EB (ELIONIX, ELS-7700). After the exposure, the films were post exposure bake (PEB) at 170 °C for 60s. They were developed by dipping THF at 23 °C for 30 s and then rinsed in deionized water for 30 s before drying. Resist patterns were recorded with a Hitachi-hitec S-5500 SEM.

3. Results and Discussion

3.1. Synthesis of Adamantane Derivative Containing Bromoalkyl Groups

The reaction of 1,3-adamantanediol and bromoacetyl bromide was carried out in the presence of DBU in NMP at 100 °C, to give a corresponding 1, 3-adamantane dibromoacetate (ADB) in 50 % yield.

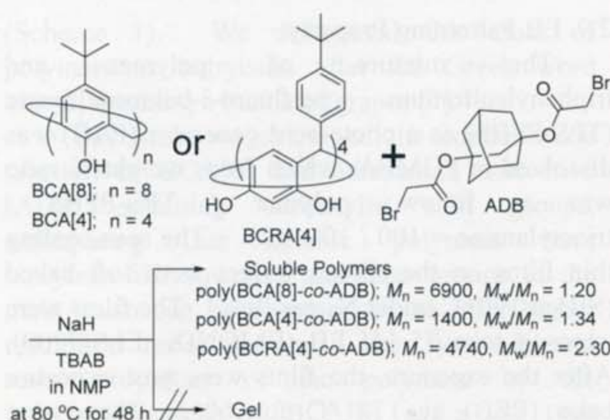
3.2. Polycondensation Reaction of *p-t*-Butylcalix[8]arene (BCA[8]), *p-t*-Butylcalix[4]arene (BCA[4]), and C-(4-*tert*-butylbenz)calix[4]resorcinarene (BCRA[4]) with 1,3-Adamantane Dibromoacetate (ADB).

The reaction of BCA[8] and ADB was carried out in the presence of DBU in NMP at 80 °C for 48h, yielding a soluble polymer poly(BCA[8]-*co*-ADB) with M_n = 6,900 and M_w/M_n = 1.20 in 19% yield (Scheme 2).

Table 1. Synthesis of poly(BCA[8]-*co*-ADB), poly(BCA[4]-*co*-ADB), and poly(BCRA[4]-*co*-ADB).[a]

Polymer	Yield (%)[b]	M_n (M_w/M_n)[c]	DR (%)[d]	T_d^i(°C)[e]	Film-forming Ability
poly(BCA[8]-*co*-ADB)	19	6,900 (1.20)	90	270	good
poly(BCA[4]-*co*-ADB)	24	1,400 (1.34)	76	283	good
poly(BCRA[4]-*co*-ADB)	78	4,740 (2.30)	70	185	good

[a]Reaction condition; at 80 °C in NMP for 48 h. [b]Methanol-insoluble part. [c] Estimated by SEC based on polystyrene standards; LiBr and phosphoric acid solution in DMF (20 mM). [d]DR; degree of reaction ratio of hydroxyl groups calculated by ^{1}H NMR spectroscopy. [e]T_d^i = Initial thermal decomposition temperature determined by TGA.



Scheme 2. Polycondensation reaction of BCA[n] (n = 4 and 8) and BCRA[4] with ADB.

Its structure was confirmed by ^{1}H NMR and IR spectroscopy, which indicated that the polymer was consistent with both units of BCA[8] and ADB. The degree of reaction ratios (DR) was calculated by the decrease of integration ratios of the peaks assignable to hydroxyl groups at about 9.0 ppm in ^{1}H NMR spectroscopy. This means that the polycondensation reaction BCA[8] and ADB proceeded not to afford gel but only soluble polymer. By the consideration based on our previous report, the soluble polymer might have botryosin-type structures as shown in Scheme 1 [7], presumably because that BCA[8] has fixed cone-shaped structures in which the hydroxyl groups are located at the lower rim and their polymerization proceeded homogeneously not to three dimensional cross-linked polymers. In the same way, the reaction of BCA[4] and BCRA[4] with ADB was performed to give the corresponding soluble polymers poly(BCA[4]-*co*-ADB) with M_n = 1,400 in 24 % yield and poly(BCRA[4]-*co*-ADB) with M_n = 4,740 in 78 % yield, respectively. These conditions and results are summarized in Table 1. Furthermore, thermal stability of the synthesized polymers was determined by thermo gravimetric analysis (TGA), and their initial decomposition temperatures (T_d^i) were in the range between 184 and 270 °C. These polymers were also soluble in common organic solvents such as DMSO, DMF, THF, $CHCl_3$, and propyleneglycol monomethyl ether acetate (PGMEA). Their film-forming ability was confirmed by the spin-coating on silicon wafers from the polymers solutions in PGMEA, and it was observed that corresponding thin films with about 100nm could be obtained from their solutions in PGMEA. These results indicate that poly(BCA[8]-*co*-ADB), poly(BCA[4]-*co*-ADB), and poly(BCRA[8]-*co*-ADB) are applicable to photoresist materials.

3.3. Thickness Loss Property on the Silicon Wafer after Soaking in TMAH aq.

Next, the value of thickness of the thin films prepared from the synthesized polymers was determined by ellipsometry before and after soaking in TMAH aq. for 30 sec, anticipating that these polymers are applicable to positive-type resist materials. These results are summarized in Table 2. In the case of the thin films of poly(BCA[8]-*co*-ADB) and poly(BCRA[4]-*co*-ADB), no decrease of their thicknesses were observed. However, 92%-decrease was observed in the case of poly(BCA[4]-*co*-ADB). This means that poly(BCA[4]-*co*-ADB) is inappropriate for resist material.

3.4. Resist Sensitivity

From the mentioned above results on thickness loss properties after soaking in TMAH aq., poly(BCA[8]-*co*-ADB) and poly(BCRA[4]-*co*-ADB) are applicable to positive type photo lithography system using TMAH aq. as a developer. Their resist-sensitivity was examined under EUV exposure tool. Solution of these polymers in the presence of 10 wt% of TPS-Nf as a PAG were spin coated on silicon wafer to prepare corresponding thin films in the absence of a quencher with about 100 nm thickness. The postexposure baking (PEB) temperatures and time were 150 °C and 60 s, respectively. The value of the thickness of remained thin films was measured by means of ellipsometer after the lithography process. As the result, both thin films of poly(BCA[8]-*co*-ADB) and poly(BCRA[4]-*co*-ADB) were insoluble in

Table 2. The ratio of thickness lost after soaking in TMAH aq.

Polymer	poly(BCA[8]-*co*-ADB)	poly(BCA[4]-*co*-ADB)	poly(BCRA[4]-*co*-ADB)
Thickness Lost[a]	0%	92%	0%

[a]Determined by ellipsometry.

TMAH aq. solution fully after EUV exposure dose. This means that these polymers could not be applicable to positive type resist materials.

Next, we examined the possibility of that these polymers are applicable to negative-type resist materials. Solution of these polymers in the presence of 30 wt% of TPS-Nf as a PAG were prepared and their thin films were prepared in the same way as mentioned above. The value of the thickness of thin films was measured after EUV exposure dose using THF as a developer. Figure 1 depicts the sensitivity curve determined by the film-thickness on the silicon wafer.

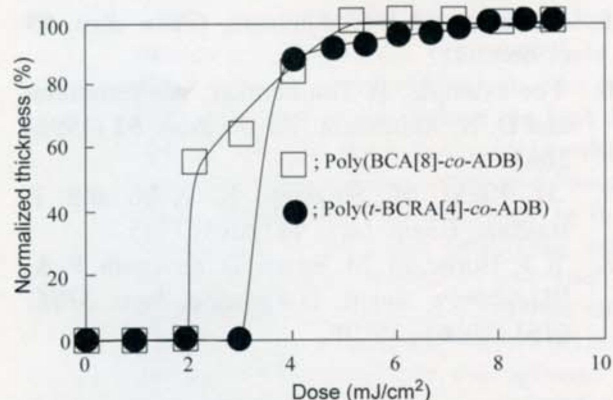


Figure 1. Resist-sensitivity curves of resist materials based on poly(BCA[8]-*co*-ADB) and poly(BCRA[4]-*co*-ADB).

Their thin-films were insoluble in THF after EUV exposure dose about 5 mJ/cm^2. This indicates that poly(BCA[8]-*co*-ADB) and poly(BCRA[4]-*co*-ADB) have adequate resist-sensitivity in the application of negative-type EUV photoresist system. Presumably because of that the synthesized polymers contained bromoalkyl groups in the side-chain, which might cause cross-linking reaction with EUV exposure to show negative-type sensitive curves.

3.5. Etching Durability

The etching durability was examined using RIE plasma process. The plasma conditions were a 15 sccm CF_4 gas flow, a 5 sccm Ar gas flow, and RF power of 100 W under 1.0 Pa pressure in the process chamber. Figure 2 depicts the etching rate of the thin films prepared from poly(BCA[8]-*co*-ADB) and poly(BCRA[4]-*co*-ADB). Polymethyl methacrylate (PMMA) and polyhydroxy styrene (PHS) were also examined as typical polymers in the application of resist materials. It was observed that poly(BCA[8]-*co*-ADB) and poly(BCRA[4]-*co*-ADB) showed good etching durability.

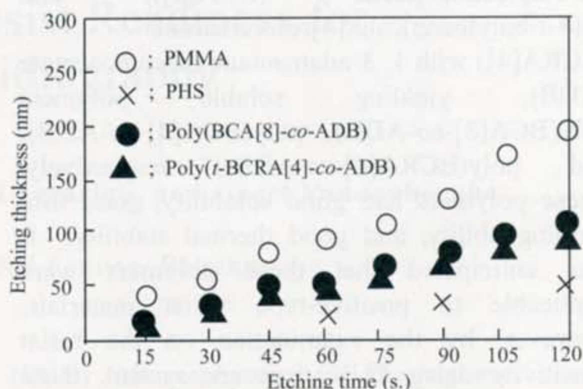
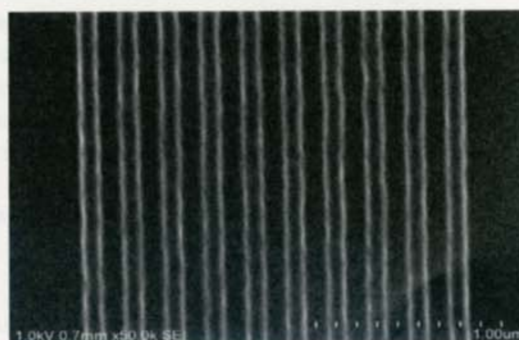


Figure 2. Etching durability of the thin films on the silicon wafer prepared from poly(BCA[8]-*co*-ADB) and poly(BCRA[4]-*co*-ADB), poly(methyl methacrylate) (PMMA), and poly(hydroxystyrene) (PHS).

3.6. EB Patterning Property

From the mentioned above results on resist sensitivity, negative resist pattern can be obtained using poly(BCA[8]-*co*-ADB) and poly(BCRA[4]-*co*-ADB). Patterning properties were examined using thin-film prepared from poly(BCRA[4]-*co*-ADB) in the EB exposure system. Figure 3 depicts SEM images of the resist pattern, which was obtained at 170 °C SB temperature and PEB temperature, and THF was used as a developer. A clear 100 nm resolution pattern with 83 nm of half-pitch was obtained using exposure dose at 640 μC/cm^2.



Line; 100 nm , Half-Pitch; 83 nm, Dose; 640 μC/cm^2

Figure 3. EB-resist patterns obtained with poly(BCRA[4]-*co*-ADB) at exposure doses at 640 μC/cm^2.

This means that the present poly(BCA[8]-*co*-ADB) and poly(BCRA[4]-*co*-ADB) would offer negative

resist pattern using THF as a developer.

In summary, we examined the condensation polymerization of *t*-butylcalix[8]arene (BCA[8]), *p-t*-butylcalix[4]arene (BCA[4]), and C-(4-*t*-butylbenz)calix[4]resorcinarene (BCRA[4]) with 1, 3-adamantane dibromoacetate (ADB), yielding soluble polymers poly(BCA[8]-*co*-ADB), poly(BCA[4]-*co*-ADB), and poly(BCRA[4]-*co*-ADB), respectively. These polymers had good solubility, good film forming ability, and good thermal stability. It was anticipated that these polymers were applicable to positive-type resist materials. However, by the examination on the resist sensitivity using EUV exposure system, these polymers were applicable to negative type resist materials using THF as a developer. Furthermore, a negative clear resist pattern with 100nm resolution could be obtained by EB exposure system. These results indicated that poly(BCA[8]-*co*-ADB) and poly(BCRA[4]-*co*-ADB) have high potential to offer higher resolution negative pattern using EUV lithography system.

Acknowledgement

This work was partly supported by Cooperative Research Program "Network Joint Research Center for Materials and Devices".

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