Poly(ether-ester) Multiblock Copolymers Based on Poly(oxymethylene-*alt*-oxyalkylene) Glycols

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Abstract : Alternating polyols of oxymethylene and oxyalkylene were synthesized and used as precursors for thermoplastic poly(ether-ester) elastomers (TPEs). The polyols were synthesized by reacting diols having different methylene units with dichloromethane in the presence of a phase transfer catalyst. The number of methylene units in the alkylene oxides was varied from 3 to 6. TPEs were prepared using the polyols as soft segments and poly(butylene terephthalate) units as hard segments. The polyols and TPEs synthesized were characterized using FTIR, NMR, GPC, DSC, and polarized optical microscopy. The polyols showed a profound odd-even effect on the melting (T_m) and glass transition temperatures (T_g). Polyols with odd numbers of methylene groups in the alkylene units have higher transition temperatures than polyols with odd number of methylene groups. The tendency is still kept in TPEs, even though the T_gs of soft segment in TPEs are slightly higher than those of corresponding neat polyols. The T_m and T_g of soft segments are almost constant in the range of 20 to 60 wt % contents of soft segments. On the other hand, the normalized heat of fusion of hard segment decreased with increasing the content of soft segment.

Keywords : poly(oxymethylene-*alt*-oxyalkylene)glycol, TPE, odd-even effect.

Introduction

Thermoplastic elastomers are one of the polymeric materials which are a commercially relevant and fundamentally interesting. They exhibit a unique combination of strength, flexibility, and processibility due to their phase-separated microstructure.[1] They are composed of two different segments, commonly referred to as soft and hard segments. The soft segments are derived from oligomers having a low T_g and are viscous at service temperature, imparting flexibility to the polymer. Interaction between the hard segments lead to phase separation in which microdomains formed serve as thermally reversible physical links. They attribute to the strength and dimension stability of the polymer. Phase separation may involve crystallization, hard segment vitrification and/or ionic clustering.

Thermoplastic poly(ether-ester) elastomers (TPEs) are multiblock copolyether esters usually composed of tetramethyleneterephthalate (PBT) units as hard segments and polyoxytetramethylene (PTMG) units as soft segments. Crystallites of PBT segments are formed on cooling from the melt and act as physical crosslinks. By varying the factors such as the ratio of hard to soft segments, the degree of

crystallinity of the hard segments and block length of soft segments they show characteristics ranging from soft elastomers to relatively hard elastoplastics. We can also control their physical properties by varying the chemical structure of hard or soft segments.

In a previous paper[2] we synthesized alternating copolymers of methylene oxide and alkylene oxide with the purpose of developing thermoplastic elastomers with improved low temperature properties. The number of methylene groups in the alkylene oxide was varied from 3 to 6. Interestingly, all the polyols prepared were crystalline and showed a profound odd-even effect on the melting (T_m) and glass transition temperatures (T_g). Polyols with the odd numbers of methylene groups in the alkylene units have higher transition temperatures than polyols with the even number of methylene groups. It is assumed that the symmetry in the polyol chains is changed with the number of methylene units and thus affects their thermal properties. An odd-even fluctuation in both melting and glass transition temperatures has been observed for several crystallizable polymers such as polyamides,[3] polyesters,[4,5] and segmented thermotropic liquid crystalline polymers.[6]

In this study, we apply the polyols to synthesize the elastomeric poly(ether-ester)s using the polyols as soft segment and investigate how the polyols affect the thermal and morphological properties of resultant TPE.

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Experimental

Materials. Diols, 1,3-propanediol(1,3-PPD), 1,4-butanediol (1,4-BD), 1,5-pentanediol(1,5-PTD), 1,6-hexanediol(1,6-HD) were purchased from Junsei Chem. Co. Tetrabutylammonium bromide(Aldrich) as phase transfer catalyst were used without further purification. Poly(oxyalkylene-*alt*-oxymethylene) glycols were used after drying at 100 °C under vacuum for 2days. Terephthaloyl chloride(Aldrich), pridine, trimethylolpropane were used after vacuum distillation. Polymerizatuion solvents were distilled and kept under 4-Å molecular sieves before using.

Synthesis of Poly(oxyalkylene-*alt*-oxymethylene) Glycols. Alternating poly(oxyalkylene-*alt*-oxymethylene) glycols were synthesized by reacting diols with dichlomethane in the presence of tetrabutylammonium bromide, a phase transfer catalyst, under basic conditions. The number of methylene units in polyols is changed from 3 to 6. The details of the reaction are described in references 2 and 3. The chemical structures of repeating units and thermal properties of the polyols are given in Table I. The polydispersity of the polyols, measured using a GPC, was in the range of 1.3 to 1.6.

Polymerizations. Prepolymers for TPE were obtained by reacting alternating polyols with terephthaloyl chloride (TPC) in chloroform in the presence of pyridine. After the reaction at 60 °C for 1 hr, a chloroform solution of 1,4-butanediol (1,4-BD) and trimethylolpropane (TMP) was added dropwise to the solution with prepolymers. The polymerization was carried out at 60 °C for the specified time. The reaction product was precipitated in methanol and washed with methanol 3 or 4 times to obtain poly(ether-ester) multiblock copolymers composed of tetramethyleneterephthalate (PBT) units as hard segments and poly(oxyalkylene-*alt*-oxymethylene) glycols as soft segments.

Characterizations. The chemical structures of polyols and the content of soft segments were characterized using a ^{1}H FT-NMR with TMS internal standard in CDCl$_3$ solvent (Bruker, 300 MHz) and an infrared spectroscopy (Nicolet 520 FTIR). Molecular weights of polyols were determined using a GPC (Waters) operated at 30 °C with THF as the mobile phase at a flow rate of 1.5 mL per min. The GPC was calibrated with a series of poly(ethylene oxide) standards. The inherent viscosity of 0.1 g/dL TPE solution in m-cresol

was measured using an Ubbelohde viscometer at 30 °C.

Thermal properties of polyols and TPEs were estimated using a differential scanning calorimeter (DSC2090, TA Instruments) at a heating rate of 5 °C/min in N$_2$ atmosphere. To apply the same thermal history, samples sealed in DSC sample pans were annealed at 100 °C under vacuum just before experiments.

The spherulitic texture of polyols and TPEs was observed using a polarizing optical microscopy (POM, Zeiss). The specimens for POM were prepared by spreading 10 wt% chloform solution onto glass substrate, then drying at 60 °C under vacuum for 24 hr, and annealing the resultant films at 100 °C for 3 hr.

Results and Discussion

Chemical Structures of TPEs. The structure of the TPEs, which are prepared using polyols, can be identified using a FTIR and a ^{1}H NMR spectroscopy. Figure 1 shows the FTIR spectra of PBT/alternating polyol block copolymers with different chemical structure. The incorporation of the PBT unit to the polyol backbone chain is certified from the strong absorption peaks at 1721 and 1270 cm^{-1}, characteristic peaks of ester linkages. The chemical structures of the block copolymers can be specified more quantitatively using a ^{1}H NMR spectroscopy. Figure 2 shows the representative ^{1}H NMR spectrum of the block copolymer from 1,6-polyol. The methylene groups in the repeating unit of the polyol and in PBT unit have characteristic chemical shifts in NMR spectrum depending on the degree of shielding of the proton attached to each methylene group. The content of soft segment in the block copolymers was estimated from the integration of the characteristic peaks corresponding to PBT and 1,6-polyol. For most cases, the content of soft segment measured is about 3 wt% lower than that expected from the molar ratio of polyol and TPC/1,4-PB. The difference would be attributed to the ring structure of chain end of polyol, not substituted to hydroxyl group. The ring structure does not participate in the reaction with TPC.

Molecular Weights of TPEs. The molecular weight of block copolymers was determined from the intrinsic viscosity of the polymers in m-cresol. The intrinsic viscosity was converted to the viscosity molecular weight using an equation

Table I. Chemical Structure and Thermal Properties of the Polyols Alternating

Polyol	Chemical Structure of Repeating Unit	T_g (°C)[a]		T_m (°C)[a]	
		3K g/mol	5K g/mol	3K g/mol	5K g/mol
1,3-polyol	-O-CH$_2$-O-CH$_2$CH$_2$CH$_2$-	-14	-12	70	71
1,4-polyol	-O-CH$_2$-O-CH$_2$CH$_2$ CH$_2$CH$_2$-	-87	-89	15	14
1,5-polyol	-O-CH$_2$-O-CH$_2$CH$_2$ CH$_2$ CH$_2$CH$_2$-	-71	-87	37	38
1,6-polyol	-O-CH$_2$-O-CH$_2$ CH$_2$ CH$_2$ CH$_2$CH$_2$CH$_2$-	-86	-90	25	26

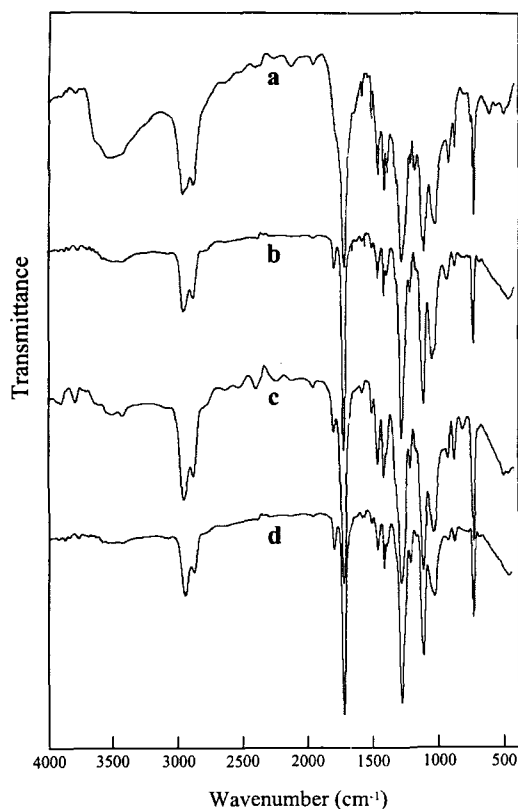[a]Measured using a DSC at the heating rate of 10 °C/min.

Figure 1. Representative FTIR spectra of PBT/alternating polyol TPE from (a) 1,3-; (b) 1,4-; (c) 1,5-; and (d) 1,6-polyols, respectively. The molecular weight of polyols is about 3,000 g/mol.

proposed by McCarthy *et al.*,[7] given as follows:

$\eta_{inh} = 0.24446 + 0.12632M_v/10,000$. The calculated values are listed in Table II. The numbers in sample code indicate the type (first two digits), the molecular weight (third digit), and the content (fourth digit) of polyol in TPE, respectively. For example, code 1424 denotes the TPE, which are prepared from 1,4-polyol with the molecular weight of 2,000 g/mol

Table II. Intrinsic Viscosity and Corresponding Viscosity Molecular Weight of TPE Prepared in This Study

Sample code	η_{inh}[a]	M_v (g/mol)[b]	Sample code	η_{inh}	M_v (g/mol)
1312	0.73	38,400	1412	0.73	38,400
1314	0.79	43,200	1414	0.52	21,800
1316	0.52	21,800	1416	0.42	13,900
1324	0.56	26,600	1424	0.61	28,900
1334	0.72	37,600	1434	0.73	38,400
1354	0.63	30,500	1454	0.70	36,100
1512	0.66	32,900	1612	0.85	47,900
1514	0.64	31,300	1614	0.63	30,500
1516	0.67	33,700	1616	0.73	38,400
1524	0.49	19,400	1624	0.57	25,800
1534	0.54	23,400	1634	0.68	34,500
1554	0.72	37,600	1654	0.56	25,000

[a]Measured at 30 °C using m-cresol as solvent.
[b]Estimated value by the equation: .

and have the 40 wt% of polyol content. Most polymers have the molecular weight in the range of 20,000 to 40,000 g/mol. The average block lengths of the hard segments can be calculated from the molecular weights of polyols used and TPE prepared. It is noteworthy that at constant molecular weight and the soft segment content, the block length of hard segments decreases as the molecular weight of soft segments increases.

DSC Characterizations. The properties of TPEs are greatly influenced by the degree of phase separation between hard and soft segments. Among various methods, DSC is considered as one of the most attractive ones for the assessments of the degree of phase separation, because it is accurate and measurements are relatively easy.[8] Assuming that TPE are composed of two distinct domains, hard and
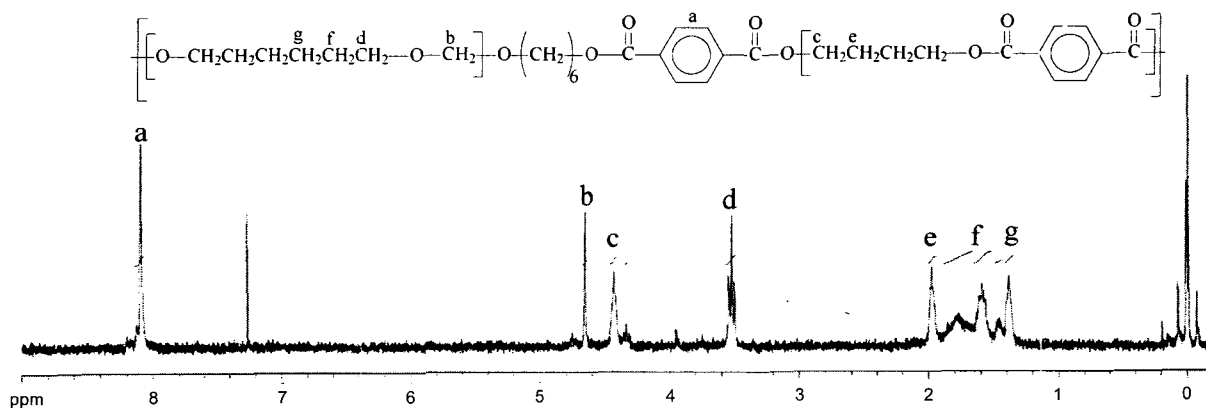

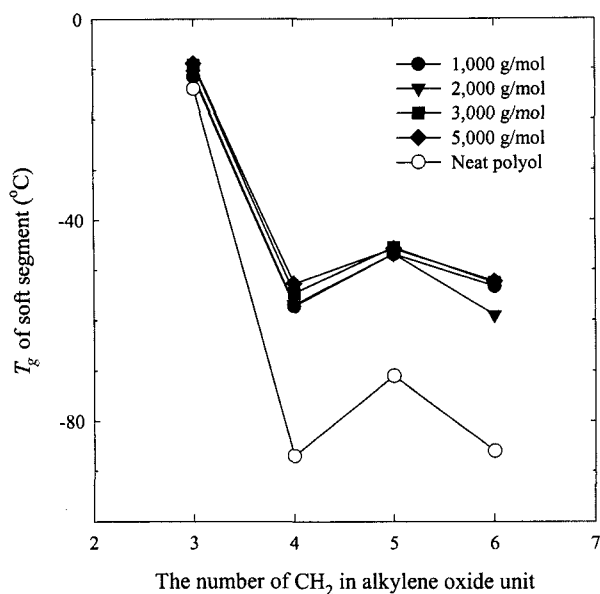**Figure 2.** Representative ^{1}H NMR spectrum for the TPE prepared from 1,6-polyol of 3,000 g/mol.

Figure 3. Effect of the number of methylene units in alkylene oxide units of alternating polyols on the T_g of soft segments. For comparison, the T_gs of neat polyols with the molecular weight of 3,000 g/mol are added.

Figure 4. Effect of soft segment content on the T_g (A) and T_m (B) of soft segments in TPE. The molecular weights of polyols are fixed at 3,000 g/mol.

soft domains, we can estimate the miscibility between the two and thus the degree of phase separation from the transition temperatures of the domains. If a fraction of hard segments is dissolved in the domain of soft segments, the T_g of soft segments in TPE will be shifted to higher values compared to that in neat polyol.

Figure 3 shows the change of the T_g of alternating polyols after TPE formation. For comparison, the T_gs of neat polyols with the molecular weight of 3,000 g/mol are added. For all cases, similarly to the glass transition behavior of neat polyols, TPEs show typical odd-even effect, indicating that the characteristics of soft segments is still preserved in TPE. However, the values of T_g are increased compared to neat polyols, indicating that PBT units are incorporated into the amorphous region of polyols. The effect of molecular weight of polyols is not significant within the molecular weight range investigated in this study.

Figure 4 shows the effect of soft segment content on the T_g and T_m of soft segments in TPE. Generally, as the block length of soft segments in TPE becomes longer, better phase separation is induced and the purity of phase-separated domains is enhanced. As a result, the values of T_g and T_m of soft segments approach to the values of neat polyols. However, as shown in Figure 4, the values of T_g and T_m of soft segments are almost constant except 1516 sample. Figure 5 shows the variation of the T_m and normalized heat of fusion (ΔH_m) of PBT units in TPE with the content of soft segment. The T_g of PBT units could not be measured because it was overlapped with T_m of soft segments. Although dependent
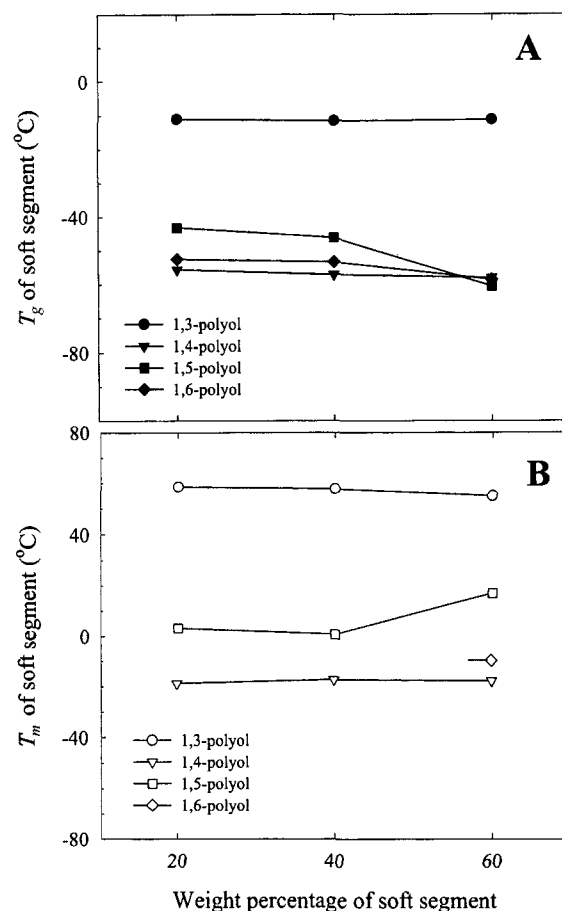
on the soft segment content, the values of the T_m of PBT units are in the range of 140 to 170 °C. Considering the T_m of commercial poly(butylene terephthalate) to be 224 °C,[8] the PBT units in TPE have the T_m about 80 °C lower than commercial PBT. This is attributed to the tiny size and imperfection of PBT crystallites, caused by the short block length and incorporation of soft segments into hard PBT domain. It is generally known that as the soft segment content increases, the T_m of hard segments decreases due to the decrease of lamellar thickness, caused by the decrease of PBT block length.[10] The experimental data shown in Figure 5A are rather confusing; a minimum of T_m of PBT unit is observed at soft segment content of 40 wt%. The difference in the conditions applied during sample preparation and measurements may affect the crystallization of PBT units and thus their melting behavior. The effect of soft segment content on the crystallization of PBT units is more clearly seen in Figure 5B. Normalized ΔH_m of PBT units, proportional to the degree of crystallinity, decreases with increasing the content of soft segment in TPE. This means that the
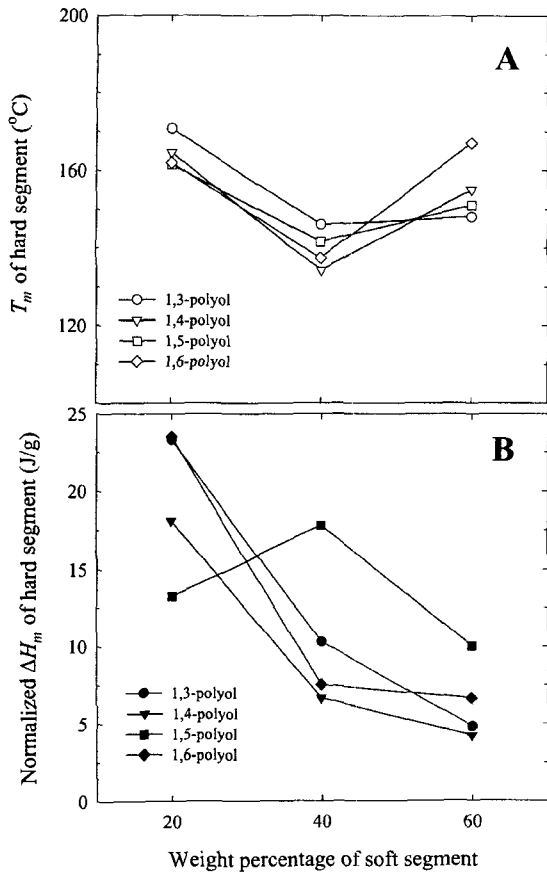
Figure 5. Variation of the T_m (A) and normalized heat of fusion (B) of PBT units in TPE with the content of soft segment. The molecular weights of polyols are fixed at 3,000 g/mol.

block length of PBT units decreases and thus the size and perfection of PBT crystallites decreases as the content of soft segments increases.

Optical Microscopy Observations. Figure 6 shows the polarizing optical micrographs of neat 1,3- and 1,5-polyols and TPEs prepared from them. The polyols were crystallized from the melt at $T_m + 20\,^{\circ}C$. The melt-crystallized polyol films form well-developed, two-dimensional spherulites with distinct Maltese cross pattern (Figures 6A and 6B). On the other hand, when the polyols are multiblock-copolymerized, distinct spherulites are almost destroyed and only small size of birefringent textures are observed for resultant TPEs, indicating that the size of polyol crystallites is significantly decreased. This results from the hindrance of crystallization of polyol unit by PBT units in TPEs.

Conclusions

Thermoplastic poly(ether-ester) were prepared using alternating polyols of oxymethylene and oxyalkylene as soft segments and poly(butylene terephthalate) units as hard segments. The odd-even effect observed for the polyols was still kept in TPEs, even though the T_gs of soft segment in TPEs are slightly higher than those of corresponding neat polyols. This was considered as a result of incorporation of hard PBT units into soft polyol domains. The effect of molecular weight of polyol on the thermal properties of TPE is not significant. The T_m and T_g of soft segment are almost constant in the range of 20 to 60 wt% of soft segment contents. On the other hand, the normalized heat of fusion of hard segment decreases with increasing the content of soft
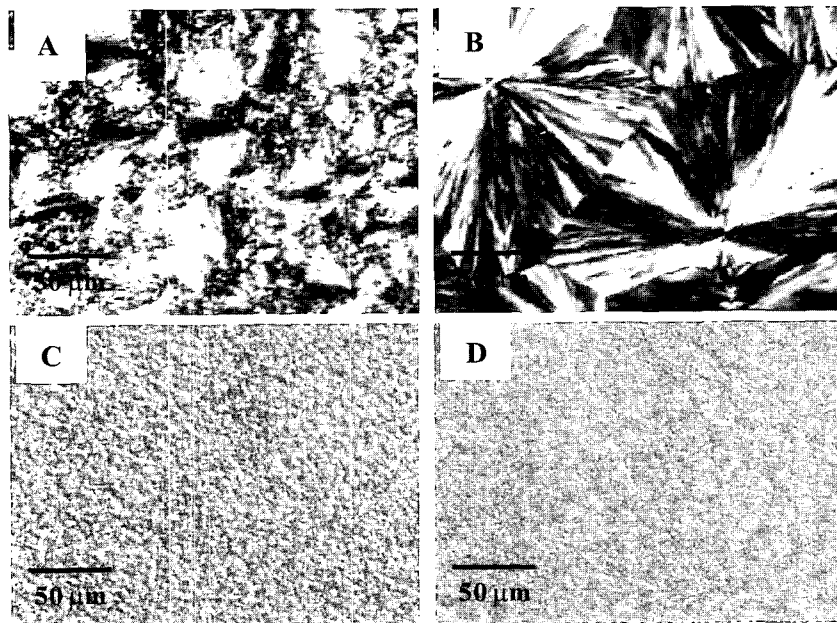

Figure 6. Transmitted polarizing optical micrographs of neat polyols and TPEs from them: (A) 1,3-polyol; (B) 1,5-polyol; (C) TPE-1334; (D) TPE-1534, repsectively. The molecular weights of polyols are 3,000 g/mol.

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Mechanical behaviours of TPEs concerned with odd-even effects will be fulfilled in the continuing research.

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