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Photochemical Synthesis of Block Copolymers of Styrene and Methylmethacrylate with the Aid of 4,4'-Azo-Bis-(4-cyano-pentane-trichloroacetylamide)

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PHOTOCHEMICAL SYNTHESIS OF BLOCK COPOLYMERS OF STYRENE AND METHYLMETHACRYLATE WITH THE AID OF 4,4'-AZO-BIS-(4-CYANO-PENTANE-TRICHLOROACETYLAMIDE)

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ABSTRACT

Polystyrene, PSt, ($M_n \approx 14\,000$) containing CCl_3 end groups was obtained by free radical polymerization of styrene, St, initiated by decomposition of azo groups of 4,4'-azo-bis-(4-cyanopentane-trichloroacetylamide), ACPT, in dimethylformamide solution at 70°C. This polymer was used as initiator for free radical polymerization of methylmethacrylate, MMA. Free radical sites located at the end of PSt chains were generated photochemically ($\lambda_{inc} = 436$ nm) with the aid of $Mn_2(CO)_{10}$. St/MMA block copolymer containing 72 to 86 mol% MMA was obtained from the crude product after extraction of unreacted PSt with boiling cyclohexane. The results demonstrate that ACPT can be applied as a bifunctional initiator for the synthesis of block copolymers of type A_nB_m or $A_nB_mA_n$, consisting of monomers A and B prone to free radical polymerization.

1. INTRODUCTION

The synthesis of block copolymers has recently become a widespread topic in polymer science in connection with the demand on novel materials possessing specific physical properties [1]. Among the various synthetic methods investigated so far the photochemical method has the advantage of being applicable at low temperatures. An elegant method was recently proposed by Simionescu et al. [2]. It is based on the use of a bifunctional low molar mass initiator containing two chromophoric groups differing significantly in optical absorptivity, namely azo and peroxide groups:

$$R-O-O-X-N=N-X-O-O-R$$

The most effective usage of these initiators was made by photolysis of the azo groups in the presence of a monomer A and subsequent thermal decomposition of the peroxide groups in the presence of a monomer B. Since the peroxide groups are contained as terminal groups in the polymer formed in the first step, a block copolymer of the structure A_nB_m is obtained in the second step. This can be seen from reactions (1) to (4):

$$R{-}O{-}O{-}X{-}N{=}N{-}X{-}O{-}O{-}R \xrightarrow{h\nu} 2\,R{-}O{-}O{-}X^{\cdot} + N_2 \qquad (1)$$

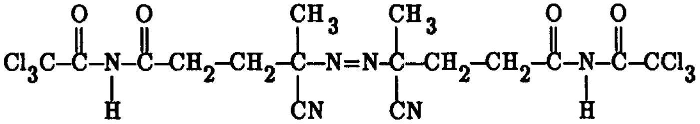
$$R{-}O{-}O{-}X^{\cdot} + nA \longrightarrow R{-}O{-}O{-}X{-}A_n^{\cdot} \qquad (2)$$

$$2\,R{-}O{-}O{-}X{-}A_n^{\cdot} \;-\!\!\left|\begin{array}{ll} \to 2\ ROO{-}X{-}A_n \ \text{(disproportionation)} & (3a) \\ \to ROO{-}X{-}A_n{-}A_{n'}{-}X{-}OOR \ \text{(combination)} & (3b) \end{array}\right.$$

$$R{-}O{-}O{-}X{-}A_n + mB \xrightarrow{\Delta} R{-}O{-}B_m + B_m{-}O{-}X{-}A_n \qquad (4)$$

Regarding reaction (4) it is notable that, apart from homopolymer $R{-}O{-}B_m$, a block copolymer of structure $B_m{-}O{-}X{-}A_n$ is formed, if termination of macroradicals comprising B moieties occurs by disproportionation. On the other hand, block copolymers of the structure $A_n{-}X{-}O{-}B_m{-}B_{m'}{-}O{-}X{-}A_{n'}$, will be formed, if termination of macroradicals occurs by combination.

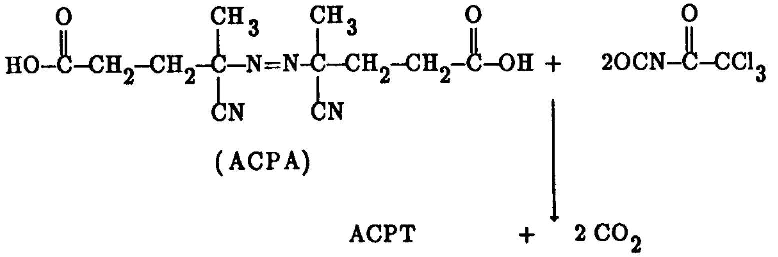
In the present paper experiments with another bifunctional initiator, 4,4'–azo–bis–(4–cyanopentane–trichloroacetylamide), ACPT, are described.



$$Cl_3C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle H}{|}}{N}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CN}{|}}{C}}{-}N{=}N{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CN}{|}}{C}}{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle H}{|}}{N}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CCl_3$$

(ACPT)

ACPT was obtained by reacting 4,4'–azo–bis–(4–cyanopentanoic acid), ACPA with trichloroacetylisocyanate



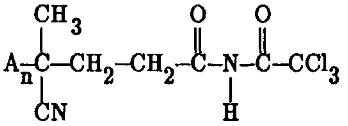
$$HO{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CN}{|}}{C}}{-}N{=}N{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CN}{|}}{C}}{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH + 2OCN{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CCl_3 \qquad (5)$$

(ACPA)

$$\downarrow$$

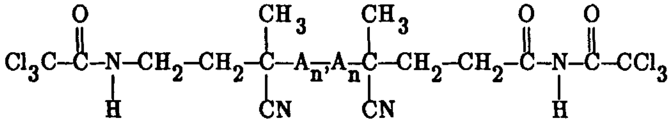
$$ACPT + 2\,CO_2$$

ACPT can be used in two modes for the synthesis of block copolymers: (a) The initiator is at first thermally decomposed in the presence of a monomer A. In this way, a polymer containing terminal CCl_3 groups of the structure



$$A_n\text{–}\underset{CN}{\overset{CH_3}{C}}\text{–}CH_2\text{–}CH_2\text{–}\overset{O}{\overset{\|}{C}}\text{–}\underset{H}{N}\text{–}\overset{O}{\overset{\|}{C}}\text{–}CCl_3$$

is formed, if termination of growing chains occurs by disproportionation. If, on the other hand, termination proceeds by combination, the resulting polymer possesses the structure



$$Cl_3C\text{–}\overset{O}{\overset{\|}{C}}\text{–}\underset{H}{N}\text{–}CH_2\text{–}CH_2\text{–}\underset{CN}{\overset{CH_3}{C}}\text{–}A_n\text{–}A_n\text{–}\underset{CN}{\overset{CH_3}{C}}\text{–}CH_2\text{–}CH_2\text{–}\overset{O}{\overset{\|}{C}}\text{–}\underset{H}{N}\text{–}\overset{O}{\overset{\|}{C}}\text{–}CCl_3$$

With the aid of this polymer, block copolymers can be obtained by applying a method proposed by Bamford [3]: the polymer is irradiated with UV light (λ: ca.350–450 nm) in the presence of $Mn_2(CO)_{10}$ and an appropriate monomer. Upon absorption of light $Mn_2(CO)_{10}$ decomposes into $Mn(CO)_5$. The latter reacts with the terminal CCl_3 groups yielding macroradicals:

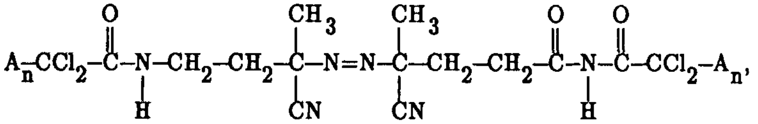
$$Mn_2(CO)_{10} + h\nu \longrightarrow 2\,Mn(CO)_5 \qquad (6)$$

$$A_n\text{–}CCl_3 + Mn(CO)_5 \longrightarrow A_n\text{–}\dot{C}Cl_2 + Mn(CO)_5Cl \qquad (7)$$

Radicals $A_n\dot{C}Cl_2$ can start the polymerization of a monomer B which is contained in the system:

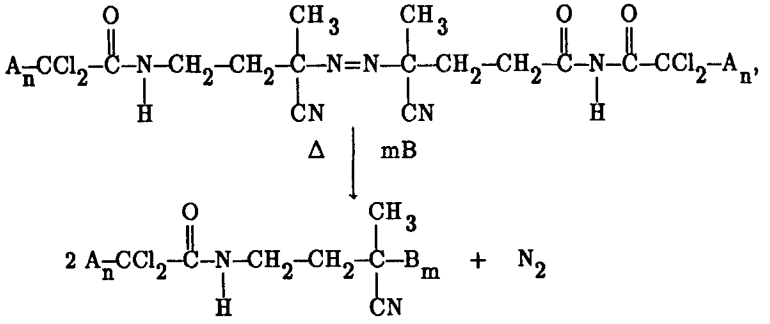
$$A_n\text{–}\dot{C}Cl_2 + mB \longrightarrow A_n\text{–}CCl_2\text{–}B_m^{\cdot} \qquad (8)$$

(b). The initiator is at first dissolved in an appropriate monomer containing $Mn_2(CO)_{10}$. Upon irradiation of the system at room temperature with UV light, that is not absorbed by the azo groups, a polymer of the following structure is formed:



$$A_n\text{–}CCl_2\text{–}\overset{O}{\overset{\|}{C}}\text{–}\underset{H}{N}\text{–}CH_2\text{–}CH_2\text{–}\underset{CN}{\overset{CH_3}{C}}\text{–}N{=}N\text{–}\underset{CN}{\overset{CH_3}{C}}\text{–}CH_2\text{–}CH_2\text{–}\overset{O}{\overset{\|}{C}}\text{–}\underset{H}{N}\text{–}\overset{O}{\overset{\|}{C}}\text{–}CCl_2\text{–}A_n,$$

This polymer can be converted into a block copolymer by heating it in the presence of a monomer B. Heating causes decomposition of the azo groups. The ensuing free radicals react with B:



$$A_n\text{-}CCl_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}\underset{\underset{H}{|}}{N}\text{-}CH_2\text{-}CH_2\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CN}{|}}{C}}\text{-}N{=}N\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CN}{|}}{C}}\text{-}CH_2\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}\underset{\underset{H}{|}}{N}\text{-}\overset{\overset{O}{\|}}{C}\text{-}CCl_2\text{-}A_{n'}$$

$$\Big\downarrow{\scriptstyle \Delta \ \mid \ mB} \qquad (9)$$

$$2\ A_n\text{-}CCl_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}\underset{\underset{H}{|}}{N}\text{-}CH_2\text{-}CH_2\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CN}{|}}{C}}\text{-}B_m \ + \ N_2$$

In the present work, method (a) was applied. At first, ACPT was reacted with styrene at 70°C. Then, the resulting polymer was mixed with methylmethacrylate and $Mn_2(CO)_{10}$ and block copolymer formation was induced by irradiating the system with UV light ($\lambda_{inc} = 436$ nm).

2. EXPERIMENTAL PART

2.1. Materials

4,4'-Azo-bis-(4-cyanopentanoic acid), ACPA, and trichloroacetylisocyanate were both obtained from Aldrich. Dimanganese decacarbonyl, $Mn_2(CO)_{10}$ (Aldrich), was purified by vacuum sublimation and stored prior to use in the dark in the refrigerator. Styrene, St, and methylmethacrylate, MMA, were freed from stabilizer and distilled. Solvents were also distilled prior to use.

2.2. Product Analysis

IR spectra were recorded with a Perkin Elmer 377 Grating Infrared spectrometer. ^1H-NMR spectra were taken in $CDCl_3$ solution using a Varian instrument, model EM 390. Tetramethylsilane served as internal standard. Gel permeation chromatograms were obtained with the aid of a Knauer instrument, model M 64, using methylethylketone as eluent. The flow rate was 1 ml/min. Molecular weights were calculated on the basis of a calibration curve recorded with polystyrene standard samples.

2.3. Synthesis of 4,4'-azo-bis-(4-cyanopentane-trichloroacetylamide, ACPT.

5 g of ACPA were dissolved in 40 ml dimethylacetamide. To this solution 10 g of trichloroacetylisocyanate was added under nitrogen at room temperature during one hour. After the mixture was stirred for two hours, the solution was divided into three portions which were poured into water. An oily product formed from which the water was decanted. The oil was dissolved in 100 ml acetone, and the solution was passed through a Kieselgel 40 column. After evaporation of the solvent 1.5 g of a white product (m.p. 127–130°C) remained corresponding to a yield of about 15 %. Elemental analysis: C: 34.2, H: 3.4, N: 14.5, Cl: 34.2 (calculated: C: 33.8, H: 2.8, N: 14.7, Cl: 37.4). The IR spectrum exhibited the characteristic carbonyl and nitrile bands at 1760 and 2240 cm^{-1}, respectively.

TABLE 1.

Polymerization of styrene in dimethylformamide at 70°C initiated by ACPT, [St]= 3.48 mol/l

Run	[ACPT] (mol/l)	Reaction Time (min.)	Conversion (%)	M_n a) (g/mol)
1	$2x10^{-2}$	60	10.5	14200
2	$2x10^{-2}$	120	15.8	14500
3	$2x10^{-2}$	180	29.3	14500
4	$2x10^{-2}$	240	36.3	14600
5	$1.0x10^{-2}$	120	18.7	10800
6	$4.1x10^{-2}$	120	30.9	5800
7	$6.2x10^{-2}$	120	30.0	5000

a) Molecular weight determined by GPC

2.4. Polymerization of Styrene

Glass ampoules with St solutions in dimethylformamide containing given amounts of ACPT were degassed on the vacuum line and sealed off. The ampoules were then heated at 70°C for a given time. Polystyrene formed was precipitated from the solution by the addition of methanol. For purification the polymer was reprecipitated from dichloromethane solutions with methanol.

2.5. Synthesis of block copolymers consisting of styrene and methylmethacrylate blocks

Polystyrene obtained as described in Section 2.4 was dissolved in a glass cuvette containing methylmethacrylate (MMA) and a small amount of $Mn_2(CO)_{10}$. A typical mixture consisted of 350 mg PSt, 1.7 mg $Mn_2(CO)_{10}$ and 5 ml MMA. Polymerization of MMA was induced by irradiation of the argon-saturated solution at $\lambda = 436$ nm. After irradiation the polymer was precipitated with methanol and dried in vacuo. Unreacted polystyrene was extracted with boiling cyclohexane. The composition of the residual block copolymer was determined by ^{1}H–NMR measurements.

3. RESULTS.

3.1. Polymerization of styrene initiated by ACPT

Polystyrene having a molecular weight of about 14000 was formed at [ACPT]= $1x10^{-4}$mol/l. As can be seen from Table 1, the conversion increased proportional to the reaction time and the molecular weight decreased upon increasing the

TABLE 2

Photopolymerisation of methylmethacrylate initiated by PSt–$CCl_3/Mn_2(CO)_{10}$ at room temperature. $[Mn_2(CO)_{10}] = 8.10^{-4}$ mol/l; Time of irradiation: 150 min (run 8 and 9) and 180 min (run 10).

Run	PSt having CCl_3 groups Conc. (g/l)	M_n (g/mol)	$[CCl_3]$ (mol/l)	Δm a) (%)	R_p b) (mol/ls)	f_{block} c)	f_{MMA} d)
8	70	14500	$9.6x10^{-3}$	42	$3.3x10^{-5}$	0.38	0.72
9	40	5800	$1.4x10^{-2}$	133	$5.9x10^{-5}$	0.67	0.86
10	40	14500	$5.5x10^{-3}$	55	$2.0x10^{-5}$	0.49	0.80

a) Relative increase in mass of polymer, $\Delta m = \frac{(m_{final} - m_{start})10^2}{m_{start}}$;

b) Rate of polymerization of MMA; c) Weight fraction of block–copolymer in product (Fraction of product insoluble in boiling cyclohexane), d) Mol fraction of MMA in block copolymer determined by NMR

ACPT concentration. Since termination occurs overwhelmingly by combination [4] in the polymerization of styrene, most macromolecules should posses two CCl_3 end groups, i.e. they should have the structure Cl_3C–PSt–CCl_3. It has to be noted, however, that values of $\delta = k_{td}/k_{tc}$ (ratio of termination rate constants for disproportionation, k_{td}, and combination, k_{tc}) reported in the literature, are at variance. Whereas most researchers concluded that $\delta \approx 0$ [4], Berger and Meyerhoff [5] reported $\delta = 0.2$, at 52°C. Therefore, it is possible that a fraction of the polystyrene obtained in this work contains only one Cl_3C group per macromolecule.

3.2 Synthesis of block–copolymers by reaction of polystyrene containing Cl_3C end groups with methylmethacrylate

Typical results obtained are shown in Table 2. Notably, R_p, the rate of MMA conversion increased almost linearly with increasing concentration of CCl_3 groups, as can be seen from Fig.1. This indicates that only a fraction of $Mn(CO)_5$ radicals generated according to reaction (6) reacted with CCl_3 groups. Actually, R_p is expected to reach a plateau value at higher concentrations of CCl_3 end groups. According to Alimoğlu et al.[6] the plateau value corresponded to concentrations

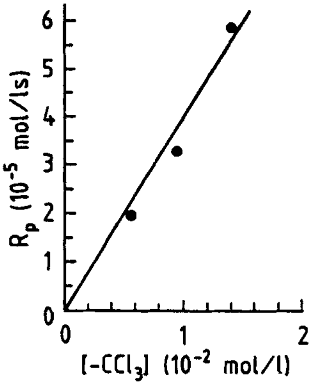


Fig.1. Polymerization of MMA initiated by PSt–CCl_3/$Mn_2(CO)_{10}$.
$[Mn_2(CO)_{10}]$= (0.8 – 1.0)10^{-3}mol/l. λ_{inc}= 436 nm.
Rate of polymerization R_p vs. concentration of CCl_3 groups.

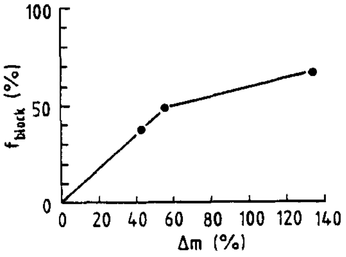


Fig.2. Photopolymerization of methylmethacrylate initiated by PSt–CCl_3/$Mn_2(CO)_{10}$. Weight fraction of block copolymer in crude polymer, f_{block}, vs. the relative increase in mass of polymer, Δm (see Table 2).

higher than about $1x10^{-2}$ mol/l when N–bromoacetyldibenz[b,f]– azepine was reacted with $Mn_2(CO)_{10}$. It seems that this compound is more reactive towards $Mn(CO)_5$ than the polystyrene having CCl_3 end groups used in this work.

As is also seen from Table 2 the total mass of polymer increased during the reaction. That this increase reflects the formation of block copolymer was concluded on the basis of the following tests: the crude product was extracted with boiling cyclohexane. In this way, unreacted polystyrene was separated from the crude polymer. The residual polymer was characterized by ^{1}H–NMR measurements which yielded MMA contents of 72 to 86 mol %. This is shown in

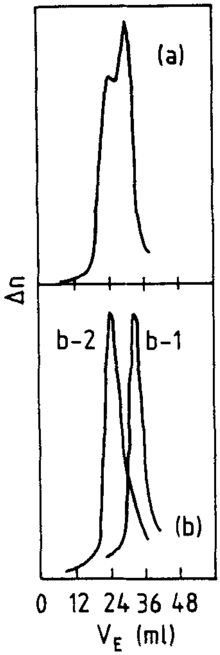


Fig.3 Gel permation chromatograms recorded with ethylmethylketone solutions. (a) Crude product obtained by reaction of PSt–CCl_3 with MMA (see Table 2, run 9). (b) Fraction of crude product soluble in boiling cyclohexane (b–1) and fraction of crude product insoluble in boiling cyclohexane (b–2, block copolymer).

the last column of Table 2. f_{block}, the fraction of residual polymer contained in the crude product, increased with increasing Δm, the relative increase in mass. This is demonstrated in Fig.2, where f_{block} is plotted vs. Δm. Block copolymer formation was also evidenced by gel permeation chromatography. Chromatograms recorded with the crude product and with the polymer fractions, obtained by extraction, are shown in Fig.3(a) and 3(b), respectively. The chromatogram of the former consists of two peaks: one at low elution volume (high molecular weight) pertaining to block copolymer and one at high elution volume pertaining to unreacted polystyrene. This assignment was arrived at on the basis of the chromatograms shown in Fig.3(b) which were obtained with the two polymer fractions.

CONCLUSIONS

This paper demonstrates how a bifunctional free radical initiator can be applied to produce block copolymers of two monomers that are prone to free radical polymerization. The functionalities of the initiator pertain to thermally degradable azo groups and to chlorine containing groups that can be photochemi–

cally transformed into free radicals with the aid of $Mn_2(CO)_{10}$ Decomposition of the azo groups in the presence of a monomer leads to macromolecules having chlorine containing end groups. Upon reaction of the latter with $Mn(CO)_5$ radical sites are formed only at the macromolecules. No additional free radicals are produced in this reaction which can initiate homopolymerization. This is the great advantage of the method applied here over other methods where the decomposition of functional groups leads, apart from macroradicals, also to isolated small radicals capable of initiating homopolymerization. In principle, homopolymerization is also feasible in the present case, namely, on the basis of chain transfer to monomer:

$$P_n^{\cdot} + M \xrightarrow{k_{tr,M}} P_n + M^{\cdot} \qquad (10)$$

($P_n^{\cdot}$: macroradical; M: monomer)

However, initiation of homopolymerization on the basis of reaction (10) is very unlikely here, because the transfer constant to monomer, C_M, is very low in the case of MMA : $C_M = k_{tr,M}/k_p \approx 1\times10^{-5}$ [7].

Regarding the homogeneity of block copolymers produced according to the method applied in this work it must be emphasized that homopolymerization is only one complicating factor. Other complications may arise from the fact that, in many cases, termination occurs both by combination and disproportionation. For the present case this implies, with $\delta = (k_{td}/k_{tc}) = 2.0$ for MMA [8], the formation of block copolymers of a variety of structures. Starting with Cl_3C–PSt–CCl_3 and assuming termination of MMA polymerization by disproportionation, the block copolymer should have the structure: *b*–MMA–*b*–St–*b*–MMA. Starting again with Cl_3C–PSt–CCl_3, but assuming termination of MMA polymerization by combination ,the formation of block copolymers having rather long chains may be envisaged, e.g.:

b–MMA–*b*–St–*b*–MMA—*b*–MMA–*b*–St–*b*–MMA

or *b*–MMA–*b*–St–*b*–MMA—*b*–MMA–*b*–St–*b*–MMA
|
b–MMA–*b*–St–*b*–MMA—*b*–MMA–*b*–St–*b*–MMA

Our GPC measurements did not reveal the formation of block copolymers of very high molecular weight. This might be due to the fact that the termination rate constants depend on the chain length, and that this dependence is not the same for the two processes, i.e. that combination becomes less probable as the chain length increases. It appears that the elucidation of this aspect deserves further investigations.

ACKNOWLEDGEMENT

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