



## Observation and Analysis of a Slow Termination Process in the Atom Transfer Radical Polymerization of Styrene

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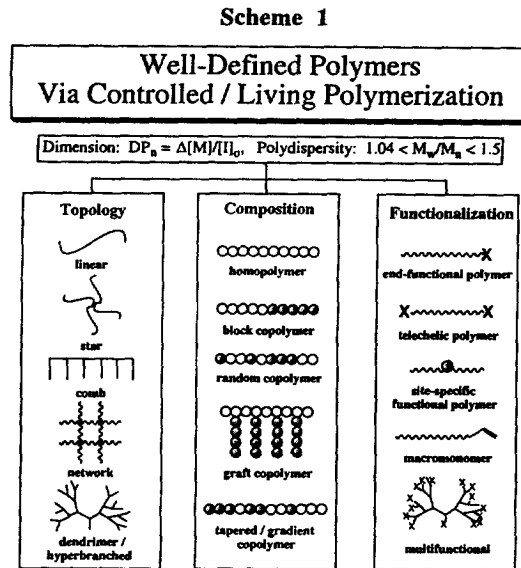
**Abstract:** Under conditions in which the rate of polymerization is slow, we have observed the slow elimination of HBr from the polymer endgroups in the ATRP of styrene. Experimental evidence indicates that this process is likely due to the solvent effect on the stability of 1-PEBr at 110 °C. A second elimination reaction was observed in a hydrocarbon solvent. The major contribution to the second elimination process comes from the reaction of the Cu(II) species, formed after atom transfer, with the growing polymeric radical which presumably occurs via a one electron oxidation process. The bimolecular rate constant for the reaction of the growing polymeric radical with the Cu(II) species in an atom transfer process is approximately  $10^3$  to  $10^4$  times greater than for the same in a termination process. Thus, the chemoselectivity for atom transfer is very high, and the effect of this termination reaction is minimal under conditions in which the concentration of monomer is high and the concentration of Cu(II) species is at the minimum necessary to ensure good molecular weight control. These data also suggest that effect of this reaction is negligible for styrene polymerizations yielding low molecular weight polymer and that it should result in an upper molecular weight limit to styrene ATRP.

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### Introduction

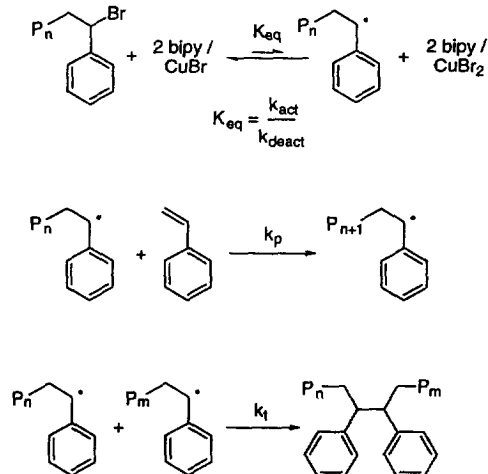
The development of new polymeric materials is predicated on the availability of methods that allow for the preparation of well-defined polymers or "controlled polymerizations." With such methods one can adjust the final average molecular weight of the polymer by varying the initial ratio of monomer-to-initiator ( $DP_n = \Delta[M] / [I]_0$ ), while maintaining a narrow molecular weight distribution ( $1.04 < M_w / M_n < 1.5$ ). Thus, using only a few monomers, one can create many new materials with vastly differing properties simply by varying the topology of the polymer (i.e., comb, star, dendritic, etc.), the composition of the polymer (i.e., random, periodic, graft, etc.), or the functionality at various sites of the polymer (i.e., end, center, side, etc.) (cf. Scheme 1).

While controlled / living radical polymerizations are a recent development in polymer synthesis, the great potential of these techniques has driven growth in their exploration and use.<sup>2,3,4,5,6</sup> Studies on these polymerization methods have led to a deeper understanding of the mechanisms by which they work,<sup>7,8</sup> which in turn has led to an increase in the extent of molecular weight control. Further understanding eventually will lead to unprecedented control and new macromolecular architectures alluded by past studies. Applications envisioned for controlled / living radical polymerizations include new specialty and commodity (co)polymers from many (or all) radically polymerizable monomers, polar: thermoplastic elastomers, surfactants, dispersants, adhesives, lubricants, solventless coatings, and hydrogels, among many possibilities.



At first glance, each of the controlled / living radical polymerization methods appears to be quite different from the other, but each functions using a common mechanistic principle: the dynamic stabilization of a reactive polymerization intermediate. For example, the mechanism of atom transfer radical polymerization (ATRP)<sup>8</sup> is shown in Scheme 2.

**Scheme 2**



In ATRP a copper(I) bromide / 2,2'-bipyridyl complex reversibly abstracts a bromine atom from a dormant polymer chain end and generates a free-radical. The polymeric radical can add monomer to elongate the polymer

chain, react with another radical in a termination step, or reabstract the bromine atom from the generated copper(II) bromide / 2,2'-bipyridyl complex. If the atom transfer equilibrium lies strongly to the side of the dormant chains ( $K_{eq} \ll 1$ ), then the steady-state concentration of radicals during the polymerization remains very low. Because propagation is first-order in radical concentration ( $k_p[R^\bullet]$ ) and termination is second-order in radical concentration ( $k_t[R^\bullet]^2$ ), at sufficiently low radical concentrations the number of chains that undergo termination during the timescale of the polymerization is insignificant. As a consequence, the polymerization displays all the characteristics of a living polymerization. Furthermore, if the atom transfer equilibrium is maintained rapidly, then the rate of exchange between dormant and active chain ends during the polymerization is sufficiently fast that all of the polymer chains add monomer at the same rate. When all of the aforementioned conditions are met, then the molecular weight distribution of the polymer chains within a given sample can be as narrow as  $M_w/M_n = 1.05$ .

ATRP and other controlled / living radical polymerizations do not meet the strict definition of a living polymerization, in that termination by coupling and disproportionation can never be suppressed completely. However, the effect of these types of termination on the polymerizations can be minimized as discussed above and will not influence the observed macroscopic control. A consequence of minimizing the fast termination steps is that much slower side reactions that are insignificant for free-radical polymerizations can have a significant effect upon the polymerization behavior of controlled / living radical polymerizations. The occurrence of these side reactions manifests itself in molecular weight distributions broader than a Poisson distribution, deceleration in the polymerization kinetics, and a limit to the maximum molecular weight achievable.<sup>9,10</sup> For a hypothetical chain growth polymerization in which only unimolecular termination occurs, the rate of termination can be several orders of magnitude slower than the rate of propagation and still limit the maximum attainable molecular weight<sup>10</sup>. Thus it is important to identify and understand slow side reactions in controlled / living radical polymerizations in order to improve the molecular weight control further. In this paper we report the observation and analysis of the slow elimination of HBr from styryl end groups in ATRP and assess the effect that this reaction has upon the polymerization.

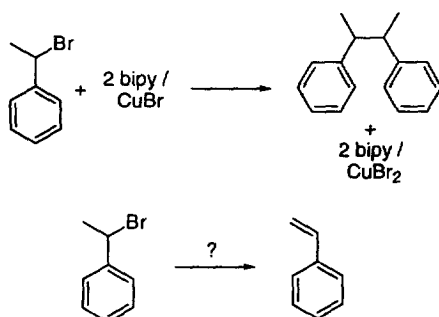
## Results and Discussion

The ATRP of styrene is well-controlled up to a molecular weight of 30,000, as evidenced by low polydispersities of approximately 1.05; above this molecular weight the polydispersities increase within the range of 1.05 to 1.50. When the ATRP of styrene is conducted under dilute conditions (50 % (v/v) or greater) at 110 °C, where the rate of polymerization is slow and the rate of thermal self-initiation is also slow, a termination process clearly can be observed.<sup>11</sup> Kinetic plots of these polymerizations exhibit deceleration with conversion, while the molecular weights ( $M_n$ ) are equal to those predetermined for a controlled process ( $DP = ([M]_0 - [M]) / [I]_0$ ). The final molecular weight distributions are also broader than in the corresponding bulk polymerizations.

In order to determine the nature of reactions involving the polymer end groups, we studied the reaction between a model end group, 1-phenylethyl bromide (1-PEBr), and the complex of CuBr with two equivalents of 4,4'-di-(5-nonyl)-2,2'-bipyridyl (dNbipy) as the catalyst. When a benzene solution of 1-PEBr and 2 dNbipy / CuBr was heated at 110 °C in a sealed NMR tube (Scheme 3),<sup>12</sup> the product of radical coupling (2,3-diphenylbutane) was formed initially. The reasons for the formation of this product were investigated

previously.<sup>8</sup> Next, the formation of styrene was observed, and its concentration increased with time. Similar results were obtained when 2 bipy / CuBr was used as the catalyst, but the reactions proceeded at a much slower rate presumably due to the lower solubility of the catalyst. A sample of the former NMR solution was analyzed using GC / MS, and a signal with a low retention time and a molecular ion peak at  $m/z = 104$  was observed, facts that are consistent with the formation of styrene as well. Thus, the formal elimination of HBr from the end group to generate an unsaturated, terminated species is implicated as a side reaction in the ATRP of styrene.

Scheme 3



Considering the above results, we undertook a series of experiments to identify the species responsible for causing the elimination of HBr. Heating 1-PEBr, alone, at 110 °C in C<sub>6</sub>D<sub>6</sub> did not result in any observed elimination even after 24 hours, so the end group is thermally stable in nonpolar media and in the absence of any component of the catalyst system. There is a significant solvent effect upon the elimination of HBr from 1-PEBr to form styrene,<sup>13</sup> and when 1-PEBr was heated in CH<sub>3</sub>CN or CH<sub>3</sub>NO<sub>2</sub>, fast formation of styrene was observed. Polar solvents, therefore, promote significant decomposition of the end group and should be avoided in the ATRP of styrene. The remaining model reactions unless specified otherwise were conducted using C<sub>6</sub>D<sub>6</sub> as the solvent.

Variable temperature NMR spectra of 2 dNbipy / CuBr in CD<sub>2</sub>Cl<sub>2</sub> showed that free and coordinated ligand exchange fast on the <sup>1</sup>H NMR timescale and that the individual signals are resolved only below 200 K. One implication of this observation is that any free ligand might accelerate the decomposition of 1-PEBr via a small polar effect, alkylation, or nucleophilic assistance in elimination. However, when two equivalents of dNbipy and one equivalent of 1-PEBr was heated at 110 °C for 24 hours no decomposition of 1-PEBr was observed. This result suggests that free ligand does not contribute to the observed termination process.

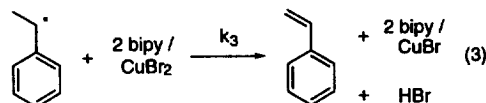
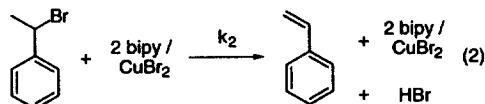
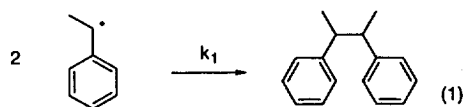
Complexes of 2,2-bipyridyl (bipy) and CuX (X = Br, Cl, PF<sub>6</sub>) exhibit a range of coordination geometries and stoichiometries, including halogen bridged dimers and monomer complexes of the formula, [(bipy)<sub>2</sub>Cu]<sup>+</sup>X<sup>-</sup>.<sup>14</sup> In those cases in which a halogen ligand becomes a counterion, X<sup>-</sup> could be sufficiently nucleophilic to catalyze the elimination of HBr from 1-PEBr. When one equivalent of tetra-*n*-butylammonium bromide or KCl / 18-crown-6 and one equivalent of 1-PEBr were heated at 110 °C, very slow elimination from

1-PEBr was observed under the former conditions and no elimination was observed under the latter conditions. Using similar reasoning, we surmised that HBr formed after elimination might catalyze the decomposition of HBr if it was not scavenged by free dipyriddy ligand. However, when 1-PEBr was heated at 110 °C for 20 hours with added concentrated HBr or  $\text{CF}_3\text{CO}_2\text{H}$ , no elimination product formed. The fact that the elimination rates were much slower in these control reactions than in the model reaction suggests that neither the counteranion of the catalyst system nor HBr contributes significantly to the observed termination process. This conclusion is further supported by the fact that model reactions using  $2 \text{ dNbipy} / [\text{Cu}(\text{CH}_3\text{CN})_4]^+ \text{PF}_6^-$  as the catalyst resulted in slightly faster elimination than when  $2 \text{ dNbipy} / \text{CuBr}$  was used.

The above experiments demonstrated that the individual components of the catalyst system were not responsible for the observed termination process, so the copper (I / II) complexes must be the source. The Cu(I) complex has been shown to be the only species that reacts with the alkyl halide end group to form radicals.<sup>8</sup> Potentially, the Cu(I) complex could also react with the radicals to form the elimination product. This possibility was examined by studying the dicumyl peroxide-initiated, free-radical polymerization of styrene with and without added  $2 \text{ dNbipy} / \text{CuBr}$ , and the polymerization kinetics, molecular weights and polydispersities were not affected by the presence of the Cu(I) complex. This result indicates that at the concentration of radicals found in ATRP there is no significant reaction between the Cu(I) species and radicals that leads to termination.

In contrast, when  $2 \text{ dNbipy} / \text{Cu}(\text{OTf})_2$  was added to dicumyl peroxide-initiated, free-radical styrene polymerizations, the polymerizations were effectively inhibited.<sup>15</sup> So, the copper (II) species formed after atom transfer appears to deactivate radicals. To confirm this premise, the model reaction was studied with varying amounts of added  $2 \text{ dNbipy} / \text{CuBr}_2$ , and the rate of formation of styrene linearly increased in proportion to the amount of added  $\text{CuBr}_2$  complex. As a control, 1-PEBr was heated at 110 °C with  $2 \text{ dNbipy} / \text{CuBr}_2$  and no Cu(I) complex. The appearance of styrene over time was observed, although the rate of formation was slower than in the corresponding reaction in which the Cu(I) complex was also present. The rate of formation of styrene also increased with an increasing concentration of Cu(II). Together, these experiments suggest that the reactions of the Cu(II) species formed after atom transfer with radicals and with 1-PEBr to form styrene are the major contributors to the observed termination process.

To assess the relative contributions of each reaction, a kinetic study was performed. Equations 1, 2, and 3 describe the three previously mentioned reactions that constitute termination, and the corresponding rate law is

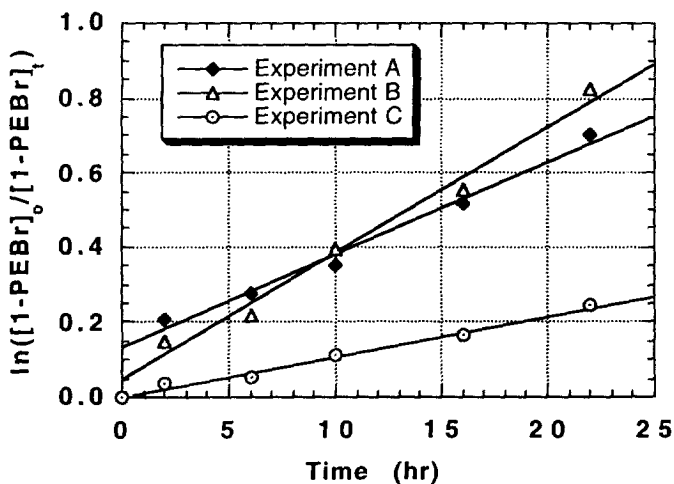


listed in equation 4. The formation of radical coupling product

$$\frac{-d[1-PEBr]}{dt} = \frac{d[\text{styrene}]}{dt} + 2 \frac{d[R-R]}{dt}$$

$$\frac{-d[1-PEBr]}{dt} = k_2 [Cu(II)] [1-PEBr] + k_3 K_{eq} [Cu(I)] [1-PEBr] + 2 k_1 [R\bullet]^2 \quad (4)$$

(Equation 1) is only significant during the initial stages of the polymerization, because the radical concentration decreases due to the corresponding rapid build up of the Cu(II) concentration with each coupling event. Thus, the third term of equation 4 is negligible after very low conversions. In order to differentiate between the other two reactions, the series of model reactions shown in Figure 1 was performed. The amount of coupling product was experimentally determined and used to calculate the actual concentrations of Cu(II) in reactions A and B. Approximately 15 % to 20 % of the coupling product was formed during the initial stages of experiment A, which translates into Cu(II) concentrations of 0.03 M to 0.04 M during the reaction. Approximately 5 % to 10 % of the coupling product was formed during the initial stages of experiment B, which revises the total concentration of Cu(II) species in the reaction to 0.04 M to 0.05 M.



**Figure 1.** Kinetics of consumption of 1-PEBr under different conditions at 110 °C in C<sub>6</sub>D<sub>6</sub>. Experiment A: [1-PEBr]<sub>0</sub> = 0.20 M; [CuBr/2dNbipy]<sub>0</sub> = 0.05 M. Experiment B: [1-PEBr]<sub>0</sub> = 0.20 M; [CuBr/2dNbipy]<sub>0</sub> = 0.05 M; [CuBr<sub>2</sub>/2dNbipy]<sub>0</sub> = 0.03 M. Experiment C: [1-PEBr]<sub>0</sub> = 0.20 M; [CuBr<sub>2</sub>/2dNbipy]<sub>0</sub> = 0.03 M.

Figure 1 shows the consumption of 1-PEBr versus time for each of the reactions. Experiment B has the fastest rate, because the concentrations of the Cu(I) and Cu(II) species are the highest of the three, while experiment C has the slowest rate for the opposite reason. In experiment C the only pathway available is equation 2, so the rate law for decomposition simplifies to  $-d[1\text{-PEBr}]/dt = k_2[\text{Cu(II)}][1\text{-PEBr}]$ . Experimentally, the rate of decomposition of 1-PEBr followed approximately first-order kinetics and correlated with the rate of formation of styrene. From this data, the rate constant for reaction 2 was measured at  $k_2 = 1.0 \pm 0.2 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$  at 110°C. The kinetics of experiments A and B are more complicated and cannot be precisely determined because the atom transfer equilibrium constant for the model reaction is not known and the concentrations of the Cu(I) and Cu(II) species vary due to the initial radical coupling reaction. Nevertheless, if one assumes that the atom transfer equilibrium constant for the model reaction is similar to that for the polymerization of styrene ( $K_{\text{eq}}(\text{styrene}) \approx 10^{-8}$ )<sup>8</sup> and that the change in concentrations of Cu(I) and Cu(II) is small after the initial radical coupling reaction, then the rate of styrene formation can be treated as a first-order dependence upon the concentration of 1-PEBr. In this manner,  $k_3$  can be estimated from the experimental data at 110 °C ( $k_3 \approx 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ). The earlier estimates of the rate constant of deactivation in ATRP (in scheme 2) indicate  $k_{\text{deact}} = 10^7$  to  $10^9 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>16</sup>

A comparison of  $k_3$  with  $k_{\text{deact}}$  shows that, in a polymerization, the growing radicals react with the Cu(II) species approximately  $10^3$  to  $10^5$  times faster in an atom transfer process than in a decomposition process. Furthermore, a comparison of  $k_3[\text{Cu(II)}][\text{R}\cdot]$  with  $k_p[\text{Styrene}][\text{R}\cdot]$  ( $k_p = 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ) shows that the effect of this termination reaction can be minimized under polymerization conditions in which the monomer concentration is high and the concentration of Cu(II) species is as low as possible while retaining molecular weight control (i.e. the conditions of bulk polymerizations). At high conversions the propagation rate becomes slower, but the rate of the side reaction does not depend upon the monomer concentration and will still proceed at the same rate. Under such conditions, the polydispersity of the final polymer may remain very low, but loss of the end group functionality may occur. Therefore, for the synthesis of block and end-functionalized polymers, the polymerization conversion must not exceed 95 % in order to prepare a well-defined polymer. The nature of the elimination reaction (Cu(II) plus radicals) can be inferred from studies on the inhibition of free-radical styrene polymerizations using metal complexes. In these studies, it was demonstrated that the metal complexes may participate in a one electron oxidation of the polymeric radical to the carbocation.<sup>17</sup> In a fast step, the carbocation subsequently eliminates a proton to form an unsaturated end group. Such a mechanism is consistent with the above observations on the termination reaction in the ATRP of styrene.

Similar side reactions also occur in other controlled / living radical polymerizations. For example, in the TEMPO-mediated polymerization of styrene<sup>7a</sup> the ratio of the rate of  $\beta$ -H abstraction to that of deactivation of the growing radical was estimated to be approximately 1-to-100, respectively.<sup>7c</sup> It is important to note that the rate of  $\beta$ -H elimination for both polymerizations may be overestimated using such model reactions due to differences in sterics and the number of  $\beta$ -protons (i.e., 3 vs. 2) between the polymer end group and the model compounds.

This ratio is similar and even slightly more than that for ATRP side reaction discussed herein. The high chemoselectivities of propagation (> 99%) in the ATRP and TEMPO-mediated styrene polymerization systems do allow for the synthesis of relatively well-defined polystyrenes when  $M_n \leq 30,000$ . Although higher molecular weight polystyrenes have been prepared using both systems, the control is usually much worse.<sup>18</sup>

In summary, we have observed a slow termination process in the ATRP of styrene. Experimental evidence from model reactions indicates that the stability of 1-PEBr at 110 °C is strongly reduced in polar solvents. The elimination reaction catalyzed by Cu(II) species was also observed in a nonpolar solvent. The major contribution to the elimination process comes from the reaction of the Cu(II) species, formed after atom transfer, with both macromolecular alkyl halide and the growing polymeric radical. The latter reaction presumably occurs via a one electron oxidation process. The bimolecular rate constant for the reaction of the growing polymeric radical with the Cu(II) species in an atom transfer process is approximately  $10^3$  to  $10^4$  times greater than for the same in a termination process. The effect of this termination reaction is minimal under conditions in which the concentration of monomer is high and the concentration of Cu(II) species is at the minimum necessary to ensure good molecular weight control. These data also indicate that effect of this reaction is negligible for styrene polymerizations yielding relatively low molecular weight polymer but it could result in an upper molecular weight limit to styrene ATRP.

### Acknowledgments

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- (12) General procedure for conducting a model reaction: In a dry box, an NMR tube was charged with the following reagents in the appropriate stoichiometries: CuBr, dNbipy, 1-phenylethyl bromide (RBr), *p*-dimethoxybenzene (an internal standard), and C<sub>6</sub>D<sub>6</sub>. The NMR tube was sealed under vacuum, and the tube was placed in an oil bath thermostatted at 110 ± 0.5 °C (or the desired temperature). At desired intervals, the tube was removed from the oil bath and cooled to room temperature (only the time the tube spent in the oil bath was counted for kinetics). <sup>1</sup>H NMR spectra were recorded using a 300 MHz Bruker NMR spectrometer.
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- (18) For example, the bulk ATRP of styrene at 110 °C allows synthesis of a polymer with a predetermined molecular weight, M<sub>n</sub> = 40,000 and M<sub>w</sub>/M<sub>n</sub> = 1.18; however when the synthesis of polystyrene of M<sub>n</sub> = 80,000 is attempted, a polymer with M<sub>n</sub> = 70,000 and M<sub>w</sub>/M<sub>n</sub> = 1.5 is obtained. At 100 °C the molecular weight control is slightly better. For example, polystyrene with a predetermined molecular weight M<sub>n</sub> = 55,300 can be prepared with M<sub>w</sub>/M<sub>n</sub> = 1.15; however when the synthesis of polystyrene with M<sub>n</sub> = 180,000 is attempted, a polymer with M<sub>n</sub> = 150,000 and M<sub>w</sub>/M<sub>n</sub> = 1.7 is obtained. Likewise, up to 91 % of the chains carry the end group from the initiator in the TEMPO-mediated polymerization of styrene at M<sub>n</sub> = 8,500, but only 65% of chains carry the initiator end group when a polymer of M<sub>n</sub> = 30,000 is prepared. The remaining chains are formed by transfer and thermal self-initiation. (Ref. 7a, 7e and Zhu, Y.; Howell, B. A.; Priddy, D. B. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **1997**, *38*(1), 97.)

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