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Atom transfer radical polymerization of methyl methacrylate with low concentration of initiating system under microwave irradiation

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Abstract

Homogeneous atom transfer radical polymerization of methyl methacrylate (MMA) under microwave irradiation (MI) with low concentration of initiating system [ethyl 2-bromobutyrate (EBB)/CuCl/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA)] was successfully carried out in *N*,*N*-dimethylformamide (DMF) at 69 °C. Plots of ln $([M]_0/[M])$ vs. time and molecular weight evolution vs. conversion showed a linear dependence. A 27.3% conversion for a polymer with number-average molecular weight (M_n) of 57,280 and a polydispersity index (PDI) of 1.19, was obtained under MI (360 W) with the ratio of $[MMA]_0/[EBB]_0/[CuCl]_0/[PMDETA]_0 = 2400/1/2/2$ in only 150 min; but 963 min was needed under conventional heating (CH) process to reach a 26.0 % conversion ($M_n = 63,990$ and PDI = 1.14) under identical polymerization conditions, indicating a significant enhancement of the polymerization rate under MI.

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Keywords: Atom transfer radical polymerization (ATRP); Microwave; Irradiation

1. Introduction

Atom transfer radical polymerization (ATRP) is one of the most convenient methods to synthesize well-defined low molecular weight polymers [1–7]. It has many advantages, such as easily available materials, remarkable tolerance of functional group [8,9], mild polymerization conditions and great industrialization prospects in comparison with other processes of living polymerization. However, the main drawbacks of ATRP are the large amount of catalyst needed and low reactivities of initiating system. Usually, a high temperature (90–130 °C) and a high concentration of catalyst and initiator are required for a high polymerization rate. One of the keys to studying ATRP, therefore, is, on the premise of 'living'/controlled polymerization, to reduce the amount of catalyst and to lower polymerization temperature. The following two ways may be able to solve the problems: developing a new catalytic system with high reactivity or enhancing the reactivities of present initiating system of ATRP by some additional measures.

It is known that microwave irradiation (MI) can accelerate chemical reactions. As to the reason of acceleration, some authors contributed it to the 'specific microwave effect' [10,11], others then contributed it to the 'dielectric heating effect' [12], but many results [13–15] have shown that, in comparison with conventional heating process (CH), reactions under MI has the advantages of higher reaction rate and greater yield of polymer within a shorter period of time; in other words, MI may act as the additional measures mentioned above.

Generally, homogeneous ATRP was conducted under some expensive and special ligands (such as, 4,4′-di-*n*-heptyl-2,2′-bipyridine (dHbipy), 4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy) and *N*-(*n*-hexyl)pyridylmethanimine (NHPMI), etc.). On homogeneous ATRP of MMA, Zhang [16] studied the kinetics of CuBr-mediated homogeneous ATRP of methyl methacrylate (MMA) using 2-hydroxyethyl-2-bromoisobutyrate (HEBIB) as initiator and *N*-(*n*-hexyl) pyridylmethanimine (NHPMI) as ligand and Matyjaszewski [17] studied the homogeneous controlled/living radical polymerization of methyl methacrylate (MMA) using the ATRP with CuCl/4,4′-di(5-nonyl)-2,2′-bipyridine catalytic system and diphenyl ether as the solvent.

Encouraged by the results [18] obtained from the homogeneous reverse ATRP of MMA in *N*,*N*-dimethylformamide (DMF) under pulsed microwave irradiation (PMI), using AIBN/$CuBr_2$/tetramethylethylenediamine (TMEDA)

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as an initiating system, in this work, we select cheap and commercially available PMDETA as ligand, and report the homogeneous solution ATRP of MMA in DMF under self-improved domestic microwave oven irradiation with initiating system of ethyl 2-bromobutyrate (EBB)/CuCl/ *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine(PMDETA), using the refluxing of solvent to control the polymerization temperature. Although very low concentration of initiating system and a low polymerization temperature (69 °C) were used, with the help of MI, the reactivities of reaction system were raised, the polymerization rate was then promoted, allowing reaction to process at a low concentration of catalyst and initiator.

2. Experimental part

2.1. Apparatus

The self-improved domestic microwave oven, M9D88 SANSUNG with irradiation frequency 2.45 GHz, is schematically shown as Fig. 1. MI power is adjustable within 90–900 W. In our experiment the MI power is adjustable to constant (360 W). The reactor is a two-neck bottle (500 ml) with refluxing solvent used for controlling the reaction temperature. The dry sealed glass tube filled with reaction mixture was placed into the refluxing solvent to let polymerization take place.

2.2. Materials

Methyl methacrylate (MMA) (chemically pure, Shanghai Chemical Reagent Co. Ltd.) was purified by extracting with 5% sodium hydroxide aqueous solution, followed by washing with deionized water and dried with sodium sulfate anhydrous overnight, and finally distilled in vacuo. Copper (I) chloride (CuCl) (analytical reagent, Shanghai Zhenxin Chemical Reagent Factory) was dissolved in hydrochloric acid, precipitated into a large amount of deionized water, filtered, washed with ethanol absolute, dried in vacuo. *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) (98%, Jiangsu Liyang Jiangdian Chemical Factory) was dried with 4-Å molecular sieve and distilled in vacuo. *N*,*N*-dimethylformamide (DMF) (analytical reagent, Shanghai No.1 Chemical Reagent Factory), tetrahydrofuran (THF) (analytical reagent, Shanghai Chemical Reagent Co. Ltd.), hydrochloric acid (HCl) (analytical reagent, Jiangsu Jincheng Chemical Reagent Co. Ltd.) and methanol (commercially available) were used as received.

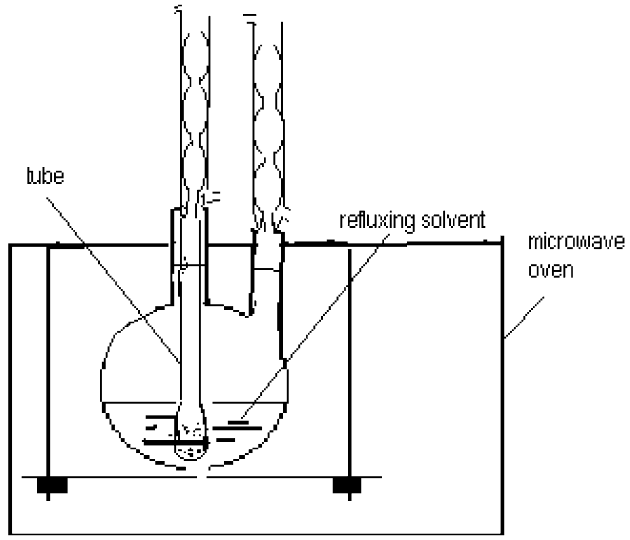

Fig. 1. Sketch map of MI experimental apparatus.

2.3. General procedures for the solution ATRP of MMA in DMF

2.3.1. MI

A typical run of the polymerization is as follows: A dry glass tube (10 ml) is filled with CuCl (3.9 mg, 0.0392 mmol), PMDETA(8.2 μl, 0.0393 mmol), DMF (1.0 ml), MMA (5.0 ml, 0.0473 mol) and EBB (2.9 μl, 0.0198 mmol) under N_2. Then, it is degassed in vacuo and charged with N_2 (three times), sealed in vacuo, and the tube is placed into the self-improved microwave oven with reflux of hexane at boiling point (69 °C). The polymerizations are stopped at a desired time by the tube being cooled in ice water. Afterward, the tube is opened and contents are dissolved in THF, precipitated into a large amount of methanol/HCl (100/0.05 v/v). The polymer is dried in vacuo until constant weight, and then weighed to give conversion.

2.3.2. CH

The sealed tube in vacuo is placed in an oil bath held by a thermostat at the desired temperature for polymerization. The other procedures are the same as those used for MI.

2.4. Characterizations

Conversion of monomer is determined by gravimetry. Molecular weights and molecular weight distributions were measured using Waters 1515 GPC with THF as a mobile phase and with column temperature of 30 °C. Polystyrene standards are used to calibrate the columns. ^{1}H NMR and ^{13}C NMR spectra are recorded in $CDCl_3$ with an INOVA 400 MHz spectrometer at ambient temperature. Glass transition temperature (T_g) is measured with Perkin–Elmer DSC-7 with the scanning rate 20 °C/min under N_2 flow (20 ml/min) using 10 mg sample.

3. Results and discussion

3.1. Effect of mole ratios of MMA/EBB/CuCl/PMDETA

Fig. 2 shows the kinetic plot of ln ([M]$_0$/[M]) vs. time for ATRP of MMA at different mole ratios of MMA/EBB/CuCl/PMDETA under MI. The resulting slopes indicate the polymerizations proceeded with an approximately constant number of active species for the duration of the polymerization. As expected, decreasing the mole ratio, namely increasing the concentrations of initiator and catalyst, increases the apparent rate constant of polymerization, k_p^{app} ($R_p = -d[M]/dt = k_p[Pn\cdot][M] = k_p^{app}[M]$), as determined from the kinetic slopes, indicating the increase of the rate of polymerization (R_p). It is noted that very low concentrations of initiator and catalyst ([EBB]$_0$/[CuCl]$_0$/[MMA]$_0$ = 1/1/3000) were used, but $k_p^{app} = 9.45 \times 10^{-5} \times s^{-1}$, indicating a high polymerization rate, can be calculated from the slope of the kinetic plot. From Fig. 2, an induction period of polymerization at low temperature (69 °C) can also be seen and become shorter (~20 min at 1200/1/1/2, ~50 min at 3000/1/1/2) with decreasing of the mole ratios. The induction period can be attributed to the establishment of equilibrium before ATRP may proceed or the consumption of residual oxygen and some impurities [19–22].

Fig. 3 shows that the molecular weight, M_n, and molecular weight distribution, M_w/M_n, as a function of conversion. PDIs at two mole ratios are narrower, $M_w/M_n <$ 1.5 (less than 40% conversion), however, increase with conversion (1.16–1.75). This can be contributed the fact that some side reactions occurred inevitably, especially, in the last step of polymerization. M_ns determined by GPC against linear polystyrene standards increase linearly with conversion, indicating that the solution polymerization of MMA in DMF under MI with EBB/CuCl/PMDETA initiation system is a living/controlled radical polymerization. From Fig. 3, it can also be seen that M_ns are close to the corresponding calculated value ($M_{n,cal}$) when the conversions are lower than 40% at two mole ratios (1200/1/1/2 and 3000/1/1/2); but when the conversion is larger than 40% (i.e. 67% at ratio of 3000/1/1/2), the $M_{n,GPC}$, is much lower than the calculated value, and the corresponding PDI becomes broader (1.75). This may contribute to the fact that MI can induce some side reactions, especially in low concentration of initiator.

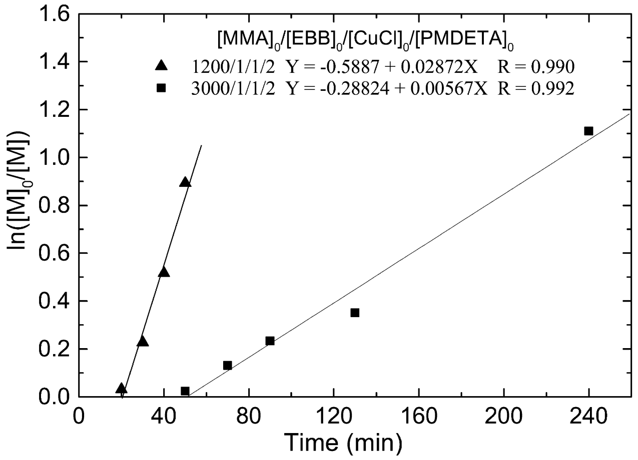

Fig. 2. Kinetics of solution ATRP of MMA in DMF under MI at different mole ratios of [MMA]$_0$/[EBB]$_0$/[CuCl]$_0$/[PMDETA]$_0$. Conditions: MMA/DMF = 5/1 (v/v); MI power = 360 W; temperature = 69 °C.

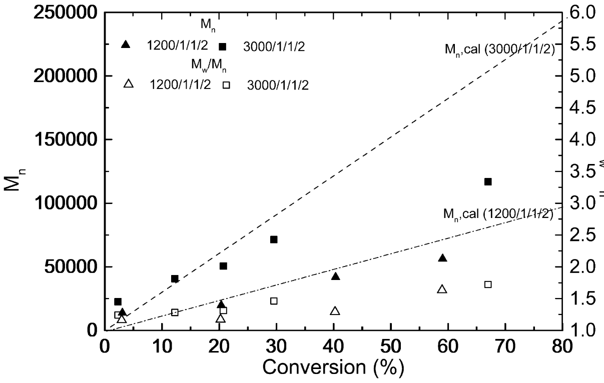

Fig. 3. Dependence of molecular weight, M_n, and molecular weight distribution, M_w/M_n, on monomer conversion in solution ATRP of MMA in DMF under MI at different mole ratios of MMA/EBB/CuCl/PMDETA. Conditions: MMA/DMF = 5/1 (v/v); MI power = 360 W; temperature = 69 °C.

3.2. Comparison of MI process with CH process

From Fig. 4, it can be seen that the rate of polymerization under MI is much faster than that under CH. The apparent constant of propagation, k_p^{app}, under CH is 1.30×10^{-5} s^{-1}; while the one under MI is 1.06×10^{-4} s^{-1}, being 8.15 times larger than that of the former. Therefore, it can be believed that MI actually accelerated the rate of polymerization. At the same time, a very long induction period (~430 min) was observed under CH process, as compared to that (~88 min) under MI. This is due to that the polymerizations

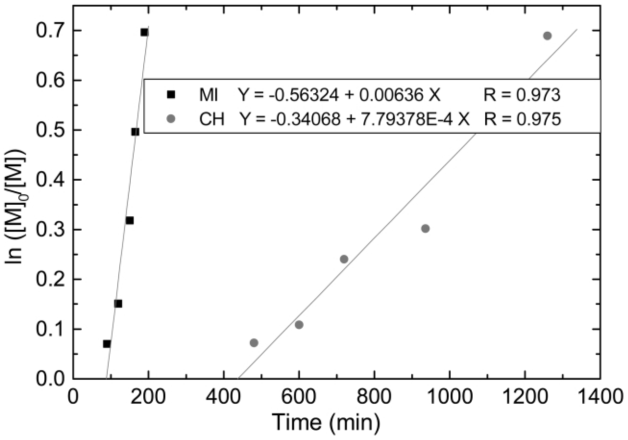

Fig. 4. Kinetics of solution polymerization of MMA in DMF under MI and CH, respectively. Conditions: [MMA]$_0$/[EBB]$_0$/[CuCl]$_0$/[PMDETA]$_0$ = 2400/1/2/2; MMA/DMF = 5/1 (v/v); temperature = 69 °C; MI power = 360 W (only for MI).

were conducted under very low concentration of initiator ($[EBB]_0/[MMA]_0 = 1/2400$) and low temperature (69 °C), leading to a slow polymerization rate, thus a long time needed to establish the dynamic equilibrium between the active species and dormant species. However, the induction period can greatly be shorted due to the significant enhancement of polymerization rate under MI. It can be believed that, under MI, the molecules in reaction system would rotate and oscillate at a high speed, then become polarized and even deformed; this could enhance the reactivities of reaction system, resulting in the acceleration of the polymerization process [18].

Fig. 5 shows the dependences of M_n and M_w/M_n on monomer conversion in solution ATRP of MMA in DMF under MI and CH, respectively. M_ns are close to the corresponding calculated M_n(cal), indicating high initiator efficiency in these polymerization conditions. Furthermore, the M_ns obtained under MI are lower than those under CH and calculated value, and PDIs are apparently broader than that under CH. This indicates MI induced side reactions. Though the polymerization was accelerated, new initiating species might be produced by MI.

3.3. T_g and stereochemistry of PMMA prepared by MI process and CH process

To better understand the effect of polymerization process, the stereochemistry of PMMA was investigated. Figs. 6 and 7 show the ^{13}C NMR spectra of PMMA prepared using EBB/CuCl/PMDETA as an initiation system under CH and MI, respectively. Both spectra are almost identical. The tacticity of PMMA was calculated from ^{13}C NMR of the quaternary carbon group (C2) [23,24].

According to the integral area of peaks of I, H and S in C2, the stereoregularity of PMMA can be calculated as shown in Table 1. From Table 1, it can be seen that all PMMA synthesized by ATRP are predominately syndiotactic (S; 57.9% under MI, 62.6% under CH), next to the heterotactic (H; 38.1% under MI, 34.3% under CH) and isotactic (I; 4.0% under MI, 3.1% under CH), and the corresponding values of S, H and I almost have the same composition, indicating MI has little effect on the structure of PMMA. As compared with the results (listed in Table 1) by conventional free radical polymerization (RP) [25], ones by ATRP both under MI and CH indicate that the same type of active species is presented in ATRP and conventional radical system.

Results of the DSC analysis of PMMA under different polymerization processes are shown in Table 2. From Table 2, all T_gs are almost same within experimental error, indicating that the effect of polymerization processes on T_g of PMMA gained by ATRP is little. At the same time, it seems that M_ns have almost no effect on T_g within the range of M_ns tested. Therefore, it can be concluded that, from the results of both T_g and stereoregularity of the polymers

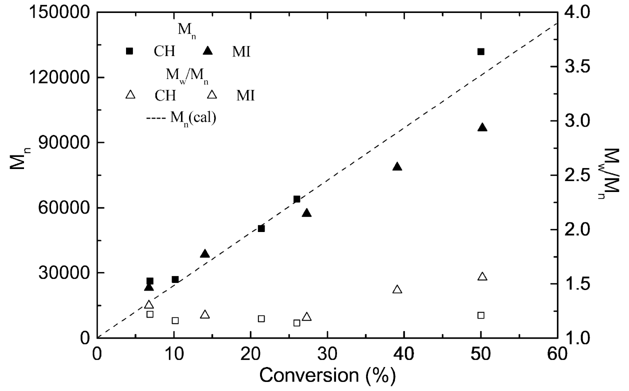

Fig. 5. Dependence of molecular weight, M_n, and molecular weight distribution, M_w/M_n, on monomer conversion in solution ATRP of MMA in DMF under MI and CH, respectively. Conditions: $[MMA]_0/[EBB]_0/[CuCl]_0/[PMDETA]_0 = 2400/1/2/2$; MMA/DMF = 5/1 (v/v); temperature = 69 °C; MI power = 360 W (only for MI).

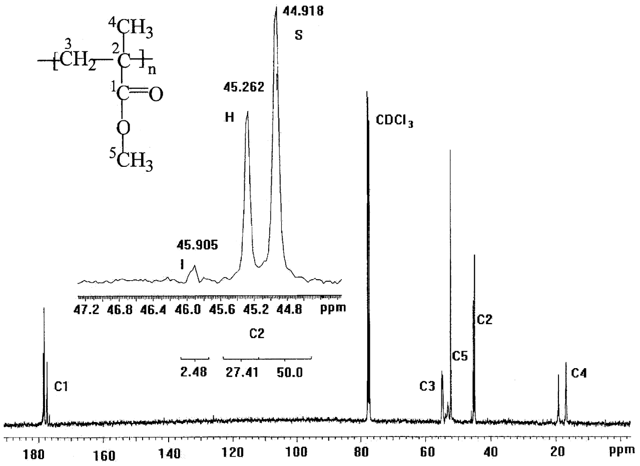

Fig. 6. ^{13}C NMR spectrum of PMMA prepared with EBB/CuCl/PMDETA as the initiating system in DMF under CH at 69 °C. Conditions: $[MMA]_0/[EBB]_0/[CuCl]_0/[PMDETA]_0 = 2400/1/2/2$; MMA/DMF = 5/1 (v/v).

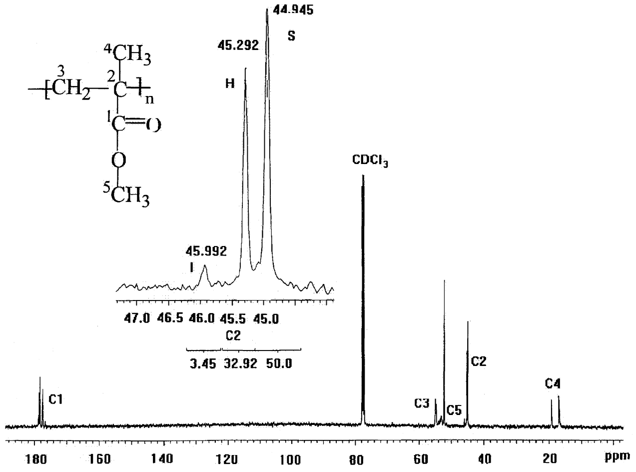

Fig. 7. ^{13}C NMR spectrum of PMMA prepared with EBB/CuCl/PMDETA as the initiating system in DMF under MI at 69 °C. Conditions: $[MMA]_0/[EBB]_0/[CuCl]_0/[PMDETA]_0 = 2400/1/2/2$; MMA/DMF = 5/1 (v/v); MI power = 360 W.

Table 1
Stereoregularity of PMMA under different polymerization processes

Polymerization process	I (%)	H (%)	S (%)
MI	4.0	38.1	57.9
CH	3.1	34.3	62.6
RP[a]	4.0	34.0	62.0

RP, conventional free radical polymerization;
[a] [MMA]o = 2.40 mol/l; initiator = AIBN; [AIBN]o = 0.02 mol/l; solvent = DMF; polymerization temperature = 60 °C.

prepared under MI and CH, the physical properties and microstructure of the polymer are not modified by the use of microwave under those cases.

3.4. Chain extension of PMMA-X

An additional method toward verifying the functionality of a polymer prepared by ATRP is its use as a macroinitiator for the same or other monomers. A chain extension of MMA with PMMA ($M_n(\mathrm{GPC}) = 16,170$, $M_w/M_n = 1.21$) as the macroinitiator was performed. The polymerization was carried out in toluene using $FeCl_2(PPh_3)_2$ as the catalyst (polymerization conditions: $[\mathrm{MMA}]_0/[\mathrm{macroinitiator}]_0/[\mathrm{FeCl_2}]_0/[\mathrm{PPh_3}]_0 = 400/1/1/2$; MMA/toluene = 2/1 (v/v); $T = 85$ °C; $t = 24$ h). The M_n for 44 % conversion of the chain-extended PMMA increased to 34,330; however, the polydispersity index (1.76) was broader than that of the macroinitiator ($M_w/M_n = 1.21$). A small part of the macroinitiator probably remained unreacted. Furthermore, the ^{1}H NMR spectrum shows a signal at 3.78 ppm corresponding to the methyl ester group at the chain end as mentioned by Sawamoto [26], which deviating the chemical shift (3.60 ppm) of other methyl ester group in PMMA due to the electron-attracting function of ω-halogen. These thus prove the fact that the mechanism of the solution ATRP of MMA in DMF initiated/catalyzed by EBB/CuCl/PMDETA is consistent with that of ATRP mentioned by Matyjaszewski [2].

4. Conclusions

Homogeneous living/controlled polymerization of MMA with the initiating system EBB/CuCl/PMDETA was achieved under MI. Plots of ln ([M]$_0$/[M]) vs. time and molecular weight evolution vs. conversion showed a linear dependence. Chain extension was performed to confirm the living/controlled nature of the polymerization system. Applying MI to the ATRP system could significantly increase the rate of polymerization, even if very low concentrations of initiator and catalyst ($[\mathrm{EBB}]_0/[\mathrm{CuCl}]_0/[\mathrm{MMA}]_0 = 1/1/3000$) and temperature (69 °C) were used, indicating the possibility of decreasing the amount of initiator and catalyst and lowering polymerization temperature.

Table 2
T_g under CH (polymerization conditions: $[\mathrm{MMA}]_0/[\mathrm{EBB}]_0/[\mathrm{CuCl}]_0/[\mathrm{PMDETA}]_0 = 2400/1/2/2$; MMA/DMF = 5/1 (v/v); temperature = 69 °C) and MI (irradiation power = 360 W; other conditions identical to polymerization conditions of CH) processes

Entry	MI		CH	
	$M_{n(\mathrm{GPC})}$	T_g (°C)	$M_{n(\mathrm{GPC})}$	T_g (°C)
1	23,160	133.3	26,280	132.2
2	57,280	131.9	83,950	133.4
3	96,610	129.1	108,160	133.2

Acknowledgements

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