typical quadratic sum of uncertainties in the sample and the local standards reference is ±20 ppm ($2\sigma_m$) for a triplicate sample analysis with the ^{146}Nd/^{144}Nd normalization. We estimated uncertainties in the mean determinations for samples and groups by weighting individual values inversely as the square of individual uncertainties. Our best estimate of the absolute value of ^{142}Nd/^{144}Nd ratio of the JSC Ames metal Nd standard is 1.138264 ± 28, normalized to ^{146}Nd/^{144}Nd = 0.724140 (*25*). A more detailed description of the method of data reduction and justification of error assignments is given in (*26*).

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Oscillating Stereocontrol: A Strategy for the Synthesis of Thermoplastic Elastomeric Polypropylene

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A strategy has been developed for the synthesis of thermoplastic elastomeric polypropylene based on the catalytic activity of the unbridged metallocene bis(2-phenylindenyl)zirconium dichloride [(2-PhInd)$_2$ZrCl$_2$]. This catalyst was designed to isomerize between achiral and chiral coordination geometries during the polymerization reaction to produce atactic-isotactic stereoblock polymers. The metallocene precursor (2-PhInd)$_2$ZrCl$_2$ in the presence of methylaluminoxane polymerizes propylene to yield rubbery polypropylene. The isotacticity of the polymer, described by the isotactic pentad content, increases with increasing propylene pressure and decreasing polymerization temperature to produce polypropylenes with an isotactic pentad content ranging from 6.3 to 28.1 percent.

The stereochemistry of polyolefins strongly influences their properties. Isotactic polypropylene, consisting of a regular arrangement of stereocenters, is a crystalline thermoplastic with a melting point of ~165°C, whereas atactic (stereorandom) polypropylene is an amorphous gum elastomer. Polypropylene consisting of blocks of atactic and isotactic stereosequences is a rubbery material with properties of a thermoplastic elastomer (*1*) (Fig. 1). Natta was the first to produce rubbery polypropylene and to interpret the elastomeric properties of this material in terms of a stereoblock structure consisting of blocks of crystallizable isotactic stereosequences and amorphous atactic stereosequences (*2*). Collette and co-workers subsequently reported improved catalysts for the synthesis of polypropylene with elastomeric properties based on the use of Zr and Ti alkyls on alumina supports (*3*), and Chien and co-workers reported the synthesis of elastomeric polypropylene using a stereorigid titanocene catalyst (*4*). Chien *et al.* proposed that polymerization occurs alternately at aspecific and isospecific coordination sites to give a stereoblock structure. Although these catalyst systems represent significant advances for the synthesis of elastomeric polypropylene, it has so far proven difficult to control the polymer structure and properties through a rational modification of the catalysts or reaction conditions.

In this report, we introduce a strategy for dynamic stereocontrol in the polymerization of α-olefins. We describe an olefin polymerization catalyst that was designed to isomerize between achiral and chiral coordination geometries in order to produce atactic-isotactic stereoblock poly(α-olefins). This strategy provides a means of controlling the distribution of isotactic and atactic stereosequences to produce polymers that exhibit a wide range of elastomeric properties depending on the reaction conditions.

The advent of homogeneous stereospecific olefin polymerization catalysts has ushered in a new era in olefin polymerization. As described in the pioneering studies of Brintzinger and co-workers (*5*), Ewen (*6*), and Kaminsky *et al.* (*7*), chiral racemic *ansa*-metallocenes produce isotactic polyolefins, whereas achiral meso isomers form atactic polyolefins (Fig. 2) (*6*, *7*). To produce stereoblock polymers, we prepared an unbridged metallocene catalyst that was designed to isomerize between chiral *rac*-like and achiral *meso*-like geometries by rotation of the indenyl ligands about the metal-ligand bond axis (*8*). A phenyl substituent on the indene ligand was chosen to inhibit the rate of ligand rotation such that it would be slower than that of monomer insertion yet faster than the time required to construct one polymer chain in order to produce atactic-isotactic stereoblock copolymers (Fig. 3) (*9*). These catalysts can thus oscillate between aspecific and isospecific coordination geometries.

The metallocene bis(2-phenylindenyl)-zirconium dichloride, (2-PhInd)$_2$ZrCl$_2$, was isolated in 82% yield from the reaction of 2-phenylindenyllithium and ZrCl$_4$ (*10*). Analysis of the complex by ^{1}H nuclear magnetic resonance (NMR) spectroscopy between 25° and −100°C was consistent with molecular C_{2v} symmetry, as commonly observed for metallocenes in rapid

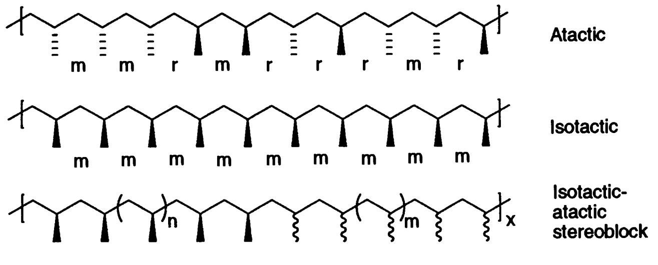

Fig. 1 (top). Isotactic, atactic, and stereoblock polypropylene (*17*).

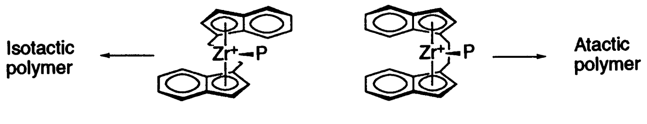

Fig. 2 (middle). Stereorigid *ansa*-metallocenes for the production of isotactic and atactic polymers.

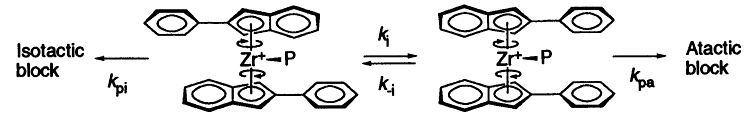

Fig. 3 (bottom). Oscillating catalyst for the production of stereoblock polymers.

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conformational equilibrium (*11, 12*).

The x-ray crystal structure of (2-PhInd)$_2$ZrCl$_2$ revealed two torsional isomers of the metallocene in the unit cell (*13*) (Fig. 4). The existence of torsional isomers in the unit cells of group IV metallocenes has been reported (*12, 14*). The phenyl substituents of racemic-like rotamer are in an *anti*-lateral conformation, whereas those of the meso-like isomer are disposed in a *syn*-lateral conformation. *Anti*-(2-PhInd)$_2$ZrCl$_2$ exhibits near C_2 symmetry. The presence of *syn* and *anti* conformations in the crystal suggests that the rotamers are energetically similar (*12*).

The catalyst derived from (2-PhInd)$_2$ ZrCl$_2$ in the presence of methylaluminoxane (MAO) is active for propylene polymerization. At a polymerization temperature of 0°C and a propylene pressure of 6.1 atm, the catalyst exhibits a productivity of 1.7×10^6 g of polymer per mole of Zr per hour. The regioselectivity of the catalyst is very high; regiomistakes (that is, 2,1-insertions) are not observable by ^{13}C NMR (*15*). The molecular weights of the polymers are also high for metallocene catalysts, a possible consequence of the high regioselectivity (*16*) (Table 1). The molecular weight distributions are in the range of $M_w/M_n = 1.5$ to 2.8, which is characteristic of single-site homogeneous catalysts (M_w is the weight-averaged molecular weight and M_n is the number-averaged molecular weight).

The productivity of the catalyst and the molecular weight of the resulting polymer are sensitive to the reaction conditions. An increase in propylene pressure results in an increase in productivity and molecular weight (samples PP5 to PP8 in Table 1). A decrease in the polymerization temperature also leads to an increase in productivity and molecular weight (PP1 to PP4). We attribute this latter behavior primarily to the increase in propylene concentration in toluene with decreasing temperature, but further studies would be required to confirm this hypothesis.

One of the most remarkable and powerful attributes of this catalyst system is the sensitivity of the polymer microstructure to the reaction conditions. The microstructure of polypropylene is commonly described in terms of the isotactic pentad content, [mmmm] (*17*), which is the fraction of stereosequences containing five adjacent isotactic stereocenters (Fig. 1). The isotactic pentad content of atactic polypropylene is 6.25%, whereas that of isotactic polypropylene can approach 100%. As shown in Table 1, [mmmm] increases with increasing propylene pressure (PP5 to PP8); [mmmm] is also quite sensitive to polymerization temperature and increases with decreasing temperature. Thus, with this catalyst system it has been possible to produce polypropylenes with an isotactic pentad content ranging from 6.3 to 28.1%. This pressure dependence is quite unusual; only three other studies that we know of report metallocene catalysts whose stereospecificities are sensitive to monomer pressure (*18*).

The sensitivity of the microstructure to the reaction conditions lends experimental support for the proposed dynamic active site model. The effect of monomer concentration ([mon]) on the microstructure of the polymer can be qualitatively predicted if it is assumed that the rate of monomer enchainment at either site is directly proportional to [mon], whereas the catalyst (cat) isomerization rate is independent of [mon] (Eq. 1)

$$\text{Isotactic block size} \propto [\text{mmmm}]$$

$$\propto \frac{\text{Isotactic enchainment rate}}{\text{Catalyst isomerization rate}} \qquad (1)$$

$$\propto \frac{k_{\text{pi}}[\text{mon}]}{k_{\text{i}}}$$

In this case, as anticipated by the kinetic model proposed by Coleman and Fox for a two-site polymerization system (*9*), the isotactic block length should increase with [mon]. The results in Table 1 (PP5 to PP8) clearly show that the isotactic block length depends on the pressure (hence [mon]) of the reaction, which provides good evidence for the proposed oscillating stereocontrol model.

Statistical modeling of the ^{13}C NMR spectra of the polypropylenes produced with this catalyst system could not be accommodated with simple Bernoullian (except for PP1, which is atactic), first- or second-order Markovian, or enantiomorphic site control propagation statistics (*19*). For a sample prepared under conditions similar to PP4 (M_w = 457,000 [mmmm] = 16%), a concurrent two-site model proposed by Zambelli *et al.* (*20*) and Chûjô and co-workers (*21*) did provide an adequate fit to the experimental spectrum where the weight fraction of isotactic stereosequences $\omega = 0.13$, the enantiomorphic site parameter $\alpha = 0.94$, and the Bernoullian parameter $\sigma = 0.51$. Fractionation of this material into refluxing solvents afforded 80% of an ether-soluble fraction ([mmmm] = 14%, M_w = 451,000) and 20% of a toluene-soluble fraction ([mmmm] = 28%, M_w = 484,000). Analysis of the ^{13}C NMR spectra of both the ether-soluble fraction ($\omega = 0.09$, $\alpha = 0.88$, $\sigma = 0.50$) and the toluene-soluble fraction ($\omega = 0.13$, $\alpha = 0.99$, $\sigma = 0.61$) were also consistent with a blocky structure (*22*). The observation that the molecular weights of all of the

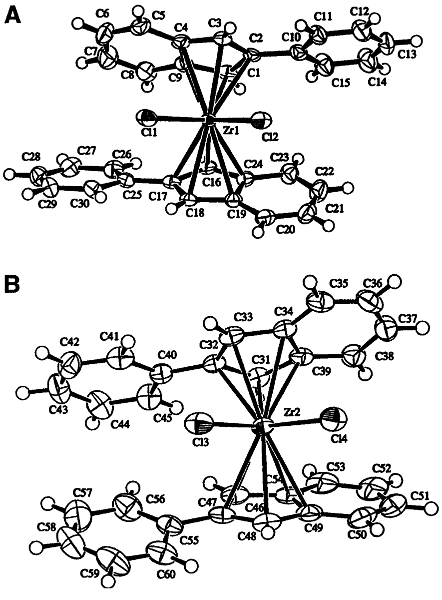

Fig. 4. Molecular structures of (**A**) *anti*- and (**B**) *syn*-rotamers of (2-PhInd)$_2$ZrCl$_2$ (crystallographic numbering scheme), with 50% probability thermal ellipsoids depicted.

Table 1. Effect of reaction temperature T_{rxn} and propylene pressure on the polymerization of propylene using (2-PhInd)$_2$ZrCl$_2$/MAO. Productivity is the number of grams of propylene per mole of Zr per hour, and [m] is the percentage of meso dyads in the polymer.

Sample	T_{rxn} (°C)	Pressure (atm)	Productivity (× 10^5)	M_w* (× 10^3)	M_w/M_n	[m]† (%)	[mmmm]† (%)
PP1‡	45	1	1.9	24	2.8	52	6.3
PP2‡	25	1	3.1	67	2.7	55	9.2
PP3‡	0	1	7.1	183	2.6	57	12.3
PP4‡	−25	1	11.0	330	2.2	60	16.1
PP5§	0	1.3	2.7	213	1.5	57	11.6
PP6§	0	2.7	6.2	395	1.9	57	13.2
PP7§	0	4.4	10.4	540	1.7	59	15.8
PP8§	0	6.1	17.3	604	1.8	61	17.4
PP9‖	−18	4.4	5.6	889	2.1	68	28.1

*Determined by gel permeation chromatography versus polystyrene. †Determined by ^{13}C NMR spectroscopy. ‡[Zr] = 1.4×10^{-4} M, [Al]/[Zr] = 1033, 15 min. §[Zr] = 5.5×10^{-5} M, [Al]/[Zr] = 1000, 10 min. ‖[Zr] = 1.1×10^{-4} M, [Al]/[Zr] = 855, 180 min.

fractions are similar suggests that these fractions are all produced by the same catalyst. The fractionation results imply that the polymers are characterized by a distribution of block lengths for the isotactic and atactic stereosequences. This is consistent with a two-site propagation mechanism, as a distribution of block lengths would be expected for a kinetically controlled process.

Several polypropylene samples formed with the $(2\text{-PhInd})_2\text{ZrCl}_2$/MAO catalyst system were analyzed by differential scanning calorimetry. Sample PP4 exhibited peak melting points at 52.1° and 78.7°C. Samples with higher [mmmm] showed higher melting points: sample PP9 exhibited a broad melting transition between 125° and 145°C with a heat of fusion of $0.4\ \mathrm{J\ g^{-1}}$. The physical properties of PP4 revealed an initial modulus of 246 psi ($17.3\ \mathrm{kg\ cm^{-2}}$), a tensile strength of 462 psi ($32.5\ \mathrm{kg\ cm^{-2}}$), and an ultimate elongation of 1210%. The elastic properties were further demonstrated by hysteresis tests, where elongation to 300% resulted in a tensile set of 50%.

REFERENCES AND NOTES

1. Thermoplastic elastomers are polymers that exhibit elastic properties yet soften and flow upon heating, unlike conventional vulcanized rubbers.
2. G. Natta, G. Mazzanti, G. Crespi, G. Moraglio, *Chim. Ind. Milan* **39**, 275 (1957); G. Natta, *J. Polym. Sci.* **34**, 531 (1959); ______ and G. Crespi, U.S. Patent 3,175,999 (1965).
3. J. W. Collette and C. W. Tullock, U.S. Patent 4,335,225 (1982); J. W. Collette *et al.*, *Macromolecules* **22**, 3851 (1989); J. W. Collette, D. W. Ovenall, W. H. Buck, R. C. Ferguson, *ibid.*, p. 3858.
4. D. T. Mallin, M. D. Rausch, Y. G. Lin, S. Dong, J. C. W. Chien, *J. Am. Chem. Soc.* **112**, 2030 (1990); J. C. W. Chien *et al.*, *ibid.* **113**, 8569 (1991).
5. F. R. W. P. Wild, L. Zsolnai, G. Huttner, H. H. Brintzinger, *J. Organomet. Chem.* **232**, 233 (1982).
6. J. A. Ewen, *J. Am. Chem. Soc.* **106**, 6355 (1984).
7. W. Kaminsky, K. Külper, H. H. Brintzinger, F. R. W. P. Wild, *Angew. Chem. Int. Ed. Engl.* **24**, 507 (1985).
8. See also G. Erker *et al.*, *J. Am. Chem. Soc.* **115**, 4590 (1993).
9. B. D. Coleman and T. G. Fox, *J. Chem. Phys.* **38**, 1065 (1963).
10. 2-Phenylindene was prepared in 64% yield by the addition of 2-indanone to phenylmagnesium bromide, followed by dehydration with *p*-toluenesulfonic acid. Deprotonation of 2-phenylindene with butyllithium yielded 2-phenylindenyllithium, which was used without further purification.
11. A.-L. Mogstad, M. D. Bruce, R. M. Waymouth, unpublished material; W. D. Luke and A. Streitwieser, *J. Am. Chem. Soc.* **103**, 3241 (1981); J. Okuda, *J. Organomet. Chem.* **356**, C43 (1988).
12. C. Krüger, M. Nolte, G. Erker, S. Thiele, *Z. Naturforsch. Teil B* **47**, 995 (1992).
13. X-ray structure analysis of $(2\text{-PhInd})_2\text{ZrCl}_2$: space group $P\bar{1}$ (no. 2), unit cell constants a = 13.538(2) Å, b = 14.553(2) Å, c = 15.365(1) Å, α = 65.78(1)°, β = 64.95(1)°, γ = 63.16(1)°, V (unit cell volume) = 2355.4(6) Å^3, d_{calc} (density) = 1.54 g cm^{-3}, μ_{calc} (absorption coefficient) = 7.1 cm^{-1}, Z (molecules per unit cell) = 4 (numbers in parentheses are the standard errors in the last digit). Total number of reflections = 8658, reflections with $[F_o^2 > 3\sigma(F_o^2)]$ = 6362, where F_o is the structure factor, R = 0.032, R_w = 0.032. During refinement, a slight disordering of the *syn* rotamer was revealed, requiring refinement at 96% occupancy. Selected bond lengths (in angstroms) for the crystographically independent rotamers: Zr(1)–Cl(1) 2.4267(9), Zr(2)–Cl(3) 2.4334(9), Zr(1)–Cl(2) 2.421(1), Zr(2)–Cl(4) 2.421(2), Zr(1)–C(1) 2.482(5), Zr(2)–C(31) 2.476(4), Zr(1)–C(2) 2.561(3), Zr(2)–C(32) 2.504(4), Zr(1)–C(3) 2.558(3), Zr(2)–C(33) 2.523(3), Zr(1)–C(4) 2.612(4), Zr(2)–C(34) 2.624(3), Zr(1)–C(9) 2.531(5), Zr(2)–C(39) 2.570(3), Zr(1)–C(16) 2.465(3), Zr(2)–C(46) 2.485(5), Zr(1)–C(17) 2.551(3), Zr(2)–C(47) 2.553(4), Zr(1)–C(18) 2.564(3), Zr(2)–C(48) 2.529(3), Zr(1)–C(19) 2.622(3), Zr(2)–C(49) 2.591(3), Zr(1)–C(24) 2.527(3), Zr(2)–C(54) 2.559(4). Selected angles for the crystallographically independent rotamers (in degrees): Cl(1)–Zr(1)–Cl(2) 95.44(4), Cl(3)–Zr(2)–Cl(4) 94.39(4), C(2)–C(1)–C(9) 107.3(3), C(32)–C(31)–C(39) 109.1(4), C(1)–C(2)–C(3) 108.0(3), C(31)–C(32)–C(33) 106.6(4), C(2)–C(3)–C(4) 108.4(4), C(32)–C(33)–C(34) 109.4(3), C(3)–C(4)–C(9) 107.8(3), C(33)–C(34)–C(39) 107.2(4), C(1)–C(9)–C(4) 108.2(4), C(31)–C(39)–C(34) 107.5(3), C(17)–C(16)–C(24) 108.2(4), C(47)–C(46)–C(54) 108.4(4), C(16)–C(17)–C(18) 107.2(3), C(46)–C(47)–C(48) 108.1(3), C(17)–C(18)–C(19) 108.8(3), C(47)–C(48)–C(49) 108.4(4), C(18)–C(19)–C(24) 107.3(4), C(48)–C(49)–C(54) 107.0(4), C(16)–C(24)–C(19) 108.2(3), C(46)–C(54)–C(49) 107.6(3), Ce–Zr(1)–Ce 131.3, Ce–Zr(2)–Ce 131.0 (Ce is the centroid of the five-membered ring).
14. C. Krüger, F. Lutz, M. Nolte, G. Erker, M. Aulbach, *J. Organomet. Chem.* **452**, 79 (1993). For an example of a related structure, K[Ti(η^6-biphenyl)$_2$], which exhibits *syn* and *anti* rotamers, see D. W. Blackburn, D. Britton, J. E. Ellis, *Angew. Chem. Int. Ed. Engl.* **31**, 1495 (1992).
15. A. Grassi, A. Zambelli, L. Resconi, E. Albizzati, R. Mazzocchi, *Macromolecules* **21**, 617 (1988); P. Corradini, V. Busico, R. Cipullo, *Makromol. Chem. Rapid Commun.* **13**, 21 (1992).
16. W. Spaleck *et al.*, *Angew. Chem. Int. Ed. Engl.* **31**, 1347 (1992).
17. Two neighboring stereocenters are described as meso (m) if they are of the same relative stereochemistry and racemic (r) if they are of opposite stereochemistry.
18. J. A. Ewen *et al.*, *Stud. Surface Sci. Catal.* **56**, 439 (1990); B. Rieger, G. Jany, R. Fawzi, M. Steimann, *Organometallics* **13**, 647 (1994); V. Busico, R. Cipullo, *J. Am. Chem. Soc.* **116**, 9329 (1994).
19. F. A. Bovey, *High Resolution NMR of Macromolecules* (Academic Press, New York, 1972).
20. A. Zambelli, P. Locatelli, A. Provasoli, D. R. Ferro, *Macromolecules* **13**, 267 (1980).
21. S.-N. Zhu, X.-Z. Yang, R. Chûjô, *Polym. J.* **15**, 859 (1983); Y. Inoue, Y. Itabashi, R. Chûjô, Y. Doi, *Polymer* **25**, 1640 (1984).
22. A.-L. Mogstad, thesis, Stanford University (1994).
23. We thank E. Moore and A. Ernst for the mechanical analysis of polymer samples, A.-L. Mogstad for carrying out polymer fractionation studies, and T. D. P. Stack for obtaining the x-ray crystal structure. We are grateful to Amoco and the National Science Foundation (grant DMR-9258324) for financial support. R.M.W. acknowledges the A. P. Sloan Foundation for a fellowship and the National Science Foundation for a National Young Investigator award, and G.W.C. acknowledges the Hertz Foundation for a fellowship.

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Segregation in DNA Solutions Induced by Electric Fields

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DNA solutions subjected to an electric field exhibit an instability that leads to DNA segregation in aggregates tilted with regard to the field. With the use of epifluorescence videomicroscopy, the evolution of DNA patterns in capillaries as a function of DNA concentration, DNA size, field strength, and field frequency was studied. The field threshold for segregation was decreased when the frequency was lowered or when the DNA molecular weight or concentration was increased. Aggregation is attributed to an electrohydrodynamic instability triggered by the dipole-dipole interaction. This phenomenon explains the failure of earlier attempts to separate large DNA in capillaries.

Molecular genetics relies heavily on the electrophoretic separation of DNA molecules by size. Until recently, this was achieved mainly in slab gels, but the joint use of capillary electrophoresis (CE) and liquid sieving media (solutions of hydrophilic polymers) has gained increasing popularity (*1*). The performances of CE for DNA fragments up to a few kilobases are excellent. Attempts to separate larger fragments have failed, however, and electrophoregrams containing many unexplained and irreproducible peaks were obtained (*2*, *3*). To investigate this question, we developed a microcapillary electrophoresis system in which the behavior of solutions containing fluorescently labeled DNA can be directly observed by intensified videomicroscopy (Fig. 1).

The first experiments were performed under a continuous field in a sieving buffer similar to those used in CE—that is, 1× TBE (89 mM tris-boric acid and 2.5 mM EDTA), 0.2% w/w hydroxypropyl cellulose (HPC; 10^6 molecular weight; Sigma), and 10 μM ethidium bromide for fluorescent labeling (*4*). Three monodisperse duplex DNA samples (bacteriophage T4, 166 kilobase pairs, Amersham, United Kingdom; bacteriophage λ, 48.5 kilobase pairs, Appligene, Illkirch F; and pBR 322, 4361 base pairs, BioLabs, Beverly, Massachusetts) were used at concentrations ranging from 0.05 to 75 μg/ml. For pBR 322, the highest concentration we studied was 25 μg/ml, and no segregation was observed in the frequen-

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