First, suppose $R = M_n(k)$. Then R is simple, and the matrix with 1's on the line above the diagonal and 0's elsewhere has minimal polynomial x^n. Conversely, suppose R is simple and has an element r whose minimal polynomial over k is $(x - a_1) \cdots (x - a_n)$, where $a_1, \ldots, a_n \in k$. Then we have a *strictly descending* chain of left ideals

$$(*)\ R \supset R(r - a_1) \supset R(r - a_1)(r - a_2) \supset \cdots \supset R(r - a_1) \cdots (r - a_n) = 0.$$

For, if $R(r - a) \cdots (r - a_i) = R(r - a_1) \cdots (r - a_{i+1})$ for some i, right multiplication by $(r - a_{i+2}) \cdots (r - a_n)$ would give $(r - a_1) \cdots (r - a_i)(r - a_{i+2}) \cdots (r - a_n) = 0 \in R$, which is impossible. Now, express R in the form $M_m(D)$ where D is a division k-algebra of, say, dimension d. Then $n^2 = m^2 d$, and ${}_R R$ has composition length m. Appealing to (*), we have $m^2 \geq n^2 = m^2 d$, so $d = 1$, $n = m$, and $R \sim M_n(k)$.