We focus only on the relative order of the following three dolls: the tallest doll (T), the shortest doll (S), and the second-tallest doll (U).

Since all painting orders are equally likely, the relative orderings of these three dolls are equally likely. There are

$$3! = 6$$

possible relative orders.

We want the shortest doll to be painted after the tallest doll, but before the second-tallest doll. That corresponds to the single ordering

$$T < S < U.$$

Thus, exactly one of the six possible relative orderings satisfies the condition.

Therefore, the desired probability is

$$\boxed{\frac{1}{6}}.$$