In 1822, Shaw drafted the first charter of the City of Boston.

Shaw married Elizabeth Knapp in 1818; she died in 1822, leaving a son and a daughter, Elizabeth, who became the wife of author Herman Melville. On August 29, 1827, Shaw remarried to Hope Savage; they had two sons.

Prior to his appointment as Chief Justice in 1829, Shaw along with Daniel Webster represented the Charles River Bridge Corporation in their attempts to stop the Warren Bridge from operating nearby. They argued that the Warren Bridge's charter of 1828 violated the Contracts Clause of the U.S. Constitution by interfering with the state's separate obligations under its charter (1785) with the Charles River Bridge proprietors, which they believed implied exclusive rights. Lawyers for the Warren Bridge proprietors contended that no exclusive rights existed for transportation over the Charles River and that judicial policy should favor technological progress and free enterprise over the rights of those of private property. After hearing oral arguments in October 1829, the Supreme Judicial Court of Massachusetts ruled in favor of the Warren Bridge proprietors. The Charles River Bridge group would later appeal the case to the U.S. Supreme Court and would lose again.

August 30, 1830 Shaw was appointed Chief State Justice by Governor Levi Lincoln, a position he held for 30 years until resigning August 21, 1860; he heard between 2,000 and 2,200 cases.

No single case brought him such criticism or such respect as the Parkman–Webster murder trial of 1850. The trial lasted eleven days with the court sitting from nine in the morning until seven in the evening. Over 60,000 spectators attended the trial. In the end it was how Justice Shaw instructed the jury that swayed the outcome. Here is the most telling part of his three hour long charge to the jury sometimes referred to as "the Webster charge":

*It has sometimes been said by judges that a jury never ought to convict in a capital case unless the dead body is found. That, as a general proposition, is true. It sometimes happens, however, that it cannot be found, where the proof of death is clear. Sometimes, in a case of murder at sea, the body is thrown overboard on a stormy night. Because the body is not found, can anybody deny that the author of that crime is a murderer?*

It took the jury less than three hours to convict Dr. John White Webster of murder. Judge Shaw passed sentence: Death by hanging.

Shaw was a judicial pioneer; his opinion often breaking from precedent. As with the Warren Bridge vs. the Charles River Bridge case, his career as a judge coincided with a crucial period in the development of America. His opinions regarding infrastructure, labor law, civil rights and criminal cases helped shape legal doctrine not only in Massachusetts but nationwide. Chief Justice Shaw was thorough, systematic, and patient, with a remarkable power to charge juries so that they understood the exact questions before them.

Widely read in English literature, he was also attracted by new mechanical processes and was a member of many learned and charitable societies. He was a fellow of Harvard College from 1834 until his death, and an Overseer from 1831 to 1853, two offices rarely united.